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ORIGINAL

First Symposium on Chemical Evolution and the Origin and Evolution of Life

Proceedings of a symposium held at
NASA Ames Research Center
Moffett Field, California
August 2-4, 1982

25th Anniversary
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NASA Conference Publication 2276

First Symposium on Chemical Evolution and the Origin and Evolution of Life

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Proceedings of a symposium sponsored by the National Aeronautics and Space Administration and the International Society for the Study of the Origin of Life and held at NASA Ames Research Center Moffett Field, California August 2-4, 1982

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Introduction

This report contains session summaries and abstracts from the "First Symposium on Chemical Evolution and the Origin and Evolution of Life," organized by Donald L. DeVincenzi, held August 2-4, 1982 at NASA' s Ames Research Center, Moffett Field, CA.

The symposium provided an opportunity for all NASA Exobiology principal investigators to present their most recent research in a scientific meeting forum. In addition, the symposium attempted to foster increased communication across disciplinary lines, formulate a more integrated program approach, review progress in all tasks, and increase visibility of the Exobiology Program.

The more than 150 participants (see Appendix) included Exobiology grantees, ARC staff, graduate students, and invited guests.

Current plans are to schedule this symposium approximately every three years as part of a series of meetings. This series might include the College Park Colloquia and meetings of the International Society for the Study of the Origin of Life.

Further information about NASA's Exobiology Program, including a yearly listing of all scientific papers from program-sponsored research, can be found in the annual "Publications of the Exobiology Program," obtainable from the NASA Headquarters Program Office.

Background

NASA's Exobiology Program seeks to understand the origin, evolution and distribution of life, and life-related molecules, on Earth and throughout the universe. The program is intriguing because of the fundamental question it addresses, complex because of the need for research in disciplines as diverse as radioastronomy and molecular biology, and scientifically sound as measured by the continued excellence of its research product.

The classic experiments of Miller and Urey, demonstrating the abiotic synthesis of essential biomolecules, were followed by a marked progression or evolution of research ideas that can be characterized as follows: precise identification of prebiotic simulation products; tests of the generality of conditions under which these syntheses occur; examination of extraterrestrial materials and environments for evidence of similar compounds and processes; adaptation of organisms to simulated extraterrestrial environments; the search for life in lunar samples, on Mars and beyond; and, probing the origin of biological structures, metabolic processes, and the genetic code. NASA-sponsored research in this area has been highlighted by several key discoveries, including demonstration of abiotic origin of meteoritic biomolecules, expansion of the range of environmental extremes over which organisms could adapt, characterization of the unusual surface chemistry on Mars, determination of earliest microbiological phylogenetic relationships, and development of the role of clays in origin of essential biopolymers.

Maintenance of a basic research program like this, in a mission-oriented agency where planetary missions to targets of exobiological significance are limited, is accomplished by focusing on the relationship between the origin of life on Earth and the origin and evolution of the solar system itself.

This relationship is explored in tasks dealing with theoretical and experimental modeling of outer planet atmospheric chemistry and implications for prebiotic syntheses, study of comets and meteorites as sources of preformed organic matter on primitive Earth, and determining mechanisms and thereby environments for abiotic production of biomolecules. The result is a program which is dependent on mission data for model validation, on the one hand, and which defines fundamental science objectives for planetary missions, on the other hand.

Although other federal agencies also support specific research tasks relevant to the origin of life, NASA's Exobiology Program is unique in several respects. It emphasizes the relationship between the origin of life and the properties of the solar system; its scope is more comprehensive as it ranges from biogenic elements to the search for extraterrestrial life; and it maintains a strong in-house technical core around which an extensive extramural program has been fashioned.

PROGRAM

Speakers are denoted with an asterisk.

Monday Morning, August 2, 1982

8:00 a.m. Registration, Foyer, N-201

8:30 a.m. Welcome - Angelo Guastaferro, Deputy Director
Ames Research Center

8:35 a.m. Conference Logistics - John Billingham
Ames Research Center

8:40 a.m. Introduction - Donald DeVincenzi
NASA Headquarters

SESSION I - EXTRATERRESTRIAL CHEMISTRY

Chairman: Sherwood Chang

8:45 a.m. (p. 38) "Accurate Theoretical Predictions of the Rotational Constants of Candidate Interstellar Molecules"

D. DeFrees*, D. McLean, and G. Loew

9:05 a.m. (p. 39) "Plasma Discharge: Meteorite Organics Model"

S. Chang, S. Gupta*, J. Lawless, R. Shipp, and T. Wydeven

9:25 a.m. (p. 40) "^{13}C NMR Spectroscopy of the Insoluble Carbon of Carbonaceous Chondrites"

J. R. Cronin*, G. U. Yuen, S. Pizzarello, and J. S. Frye

9:45 a.m. (p. 41) "Behavior and Recovery of Some Amino Acids From the Murchison Meteorite: Research in Progress"

H. Ogino and B. Nagy*

10:05 a.m. Coffee

10:15 a.m. (p. 42) "Mars' Early Climate--A Possible Habitat for Terrestrial Type Primitive Organisms"

W. R. Kuhn* and S. E. Postawko

10:35 a.m. (p. 43) "An Investigation of the Effects of Hot Atom Chemistry of Minor Constituents in the Atmospheres of Jupiter and Saturn"

T. W. Scattergood* and S. Chang

10:55 a.m. (p. 44) "Phosphine Photolysis. Applications to Jovian Atmospheric Chemistry"

J. P. Ferris*, A. Bossard, and R. Benson

11:15 a.m. (p. 45) "Photochemistry of Methane, Nitrogen and Carbon Monoxide on Titan--Abiotic Synthesis of Organic Compounds"

Y. L. Yung*, M. Allen, J. P. Pinto, and E. P. Gardner

11:35 a.m. (p. 46) "The Organic Clouds of Titan"

C. Sagan* and B. N. Khare

11:55 a.m. Lunch

Monday Afternoon, August 2, 1982

SESSION II - PRIMITIVE EARTH

Chairman: James Lawless

1:00 p.m. (p. 48) "Photochemistry of Methane in the Earth's Early Atmosphere"

J. F. Kasting, K. J. Zahnle*, and J. C. G. Walker

1:20 p.m. (p. 49) "Photochemical Reduction of Carbon Monoxide in the Earth's Primitive Atmosphere"

A. Bar-Nun and S. Chang*

1:40 p.m. (p. 50) "The Atmosphere of the Primitive Earth and the Prebiotic Synthesis of Organic Compounds"

S. L. Miller* and G. Schlesinger

2:00 p.m. (p. 51) "Chemical Evolution and Model Photosynthetic Protocells"

C. E. Folsome*

2:20 p.m. (p. 52) "Clays and the Origin of Life"

H. Hartman*

2:40 p.m. (p. 53) "The Adsorption of Biomonomers onto Homoionic Clays"

S. Bzik, F. Church, J. Lawless*, N. Levy, J. Mazzurco, and M. Mortland

3:00 p.m. (p. 54) "Catalysis of Peptide Formation on Clay Surfaces by Polyribonucleotides and by Short Peptides"

D. H. White*

3:20 p.m. Coffee

3:40 p.m. (p. 55) "Solvation/Desolvation Induced Luminescence in Kaolin--Indicator of Surface Reactivity?"

L. M. Coyne*

4:00 p.m. (p. 56) "Prebiotic Formation of Phosphoanhydrides, Like ATP, by Chemical Pathways that Resemble Fermentation (Glycolysis)"

A. L. Weber*

4:20 p.m. (p. 57) "Experiments on the Origin and Amplification of Molecular Chirality"

W. A. Bonner*

4:40 p.m. (p.58) "Absorption of Biomolecules (5'-Nucleoside Monophosphates and Amino Acids) onto Homoionic Clay Surfaces"

J. B. Orenberg*

5:00 p.m. Adjourn

Tuesday Morning, August 3, 1982

SESSION III - INFORMATION TRANSFER

Chairman: Robert MacElroy

8:30 a.m. (p. 60) "NMR Studies of Interaction Between Nucleic Acids & Proteins"

C. Ponnamperuma and M. Hobish*

8:50 a.m. (p. 61) "Cyanamide Mediated Prebiological Synthesis of Phospholipids, Oligopeptides and Oligonucleotides"

J. Oro*

9:10 a.m. (p. 62) "An RNA Polymerase Model"

L. E. Orgel*, T. Inoue, and H. Fakhrai

9:30 a.m. (p. 63) "Self-Ordering → Reverse Translation?"

S. W. Fox*, T. Nakashima, and R. M. Syren

9:50 a.m. (p. 64) "Possible Pathways Towards the Evolution of the Genetic Code"

F. R. Eirich* and M. Paecht-Horowitz

10:10 a.m. Coffee

10:30 a.m. (p. 65) "The Chemical Basis for the Origin of the Genetic Code and the Process of Protein Synthesis"

J. C. Lacey*, Jr.

10:50 a.m. (p. 66) "Nucleic Acid Template Properties"

R. Rein* and T. Kieber-Emmons

11:10 a.m. (p. 67) "The Influence of Water on the Stability of DNA Base Pairs"

A. Pohorille*, S. K. Burt, and R. D. MacElroy

11:30 a.m. Lunch

Tuesday Afternoon, August 3, 1982

SESSION IV - SOLAR SYSTEM EXPLORATION

Chairman: Glenn C. Carle

12:30 p.m. (p. 69) "New GC Columns for Investigation of the Atmospheres of Titan and the Outer Planets"

G. E. Pollock*, D. R. Kojiro, and F. H. Woeller

12:50 p.m. (p. 70) "Limits of In Situ Detection of Volatiles in Solar System Exploration"

F. H. Woeller*, D. R. Kojiro, and G. C. Carle

1:10 p.m. (p. 71) "Analysis of Cometary Dust by Gas Chromatography"

B. J. O'Hara*

1:30 p.m. (p. 72) "Multiplex Chromatography for Solar System Exploration"

J. R. Valentin*, G. C. Carle, and J. B. Phillips

SESSION V - PLANETARY PROTECTION

Chairman: Donald DeVincenzi

1:50 p.m. (p. 74) — "Proposed New Policy for Planetary Protection"

D. L. DeVincenzi, P. D. Stabekis*, and J. B. Barengoltz

2:10 p.m. — Open Discussion

2:50 p.m. — Coffee

SESSION VI - FUTURE DIRECTIONS

Chairman: John Billingham

3:10 p.m. (p. 76) — "Biogenic Elements and Their Compounds: The Astrophysical Context"

J. Wood*

3:30 p.m. (p. 77) — "Galapagos Hydrothermal Vent Ecologies: Possibilities for Neoabiogenesis?"

C. Ponnamperuma and M. Hobish*

3:50 p.m. (p. 78) — "Evolution of Complex and Higher Organisms"

D. Raup* and J. Billingham

4:10 p.m. (p. 79) — "Role of Exobiological Science in the Future of Solar System Exploration"

J. Oro*

4:30 p.m. (p. 80) — "Status of SETI Research"

F. D. Drake*

4:50 p.m. — Adjourn

7:00 p.m. Dinner

Guest Speaker

Wednesday Morning, August 4, 1982

SESSION VII - GEOLOGICAL RECORD

Chairman: David Des Marais

8:30 a.m. "Aspects of Evolution and Diversity of Precambrian Life: Archean and Proterozoic"
(p. 82)

E. S. Barghoorn* and P. K. Strother

8:50 a.m. "Archaean Stromatolites from Zimbabwe: Evidence for Environmental Conditions"
(p. 83)

P. I. Abell*, J. McClory, E. Nisbet, and A. Martin

9:10 a.m. "Geochemistry of Carbon in the Lower Crust and the History of the Carbon Cycle on Earth"
(p. 84)

D. Des Marais*

9:30 a.m. "The Oxygen Isotopic Record in Precambrian Kerogens"
(p. 85)

J. M. Hayes and K. W. Wedeking*

9:50 a.m. "Alteration Paths of Sedimentary Rock Organic Matter During Burial"
(p. 86)

I. R. Kaplan*

10:10 a.m. Coffee

10:25 a.m. "The Importance of Metal Complexed Amino Acids in Geochronology of Fossils and to the Origin of Chirality"
(p. 87)

G. G. Smith*

10:45 a.m. (p. 88) "The Origin and Evolution of Microbial Endoliths"

S. E. Campbell and S. Golubic*

11:05 a.m. (p. 89) "Organic Chemical Gradients in Laminated Cyanobacterial Mats from Solar Lake, Israel"

A. L. Burlingame*

11:25 a.m. (p. 90) "Geochemical Anomalies Near the Cretaceous-Tertiary, Eocene-Oligocene and Permian-Triassic Boundaries"

F. Asaro*, L. W. Alvarez, W. Alvarez, and H. V. Michel

11:45 a.m. Lunch

Wednesday Afternoon, August 4, 1982

SESSION VIII - EARLY BIOLOGICAL EVOLUTION

Chairman: Lawrence Hochstein

1:00 p.m. (p. 92) "Microbial Mats and Early Evolution"

L. Margulis* and J. F. Stolz

1:20 p.m. (p. 93) "Evolutionary Relationships in the Microbial World"

G. E. Fox* and C. R. Woese

1:40 p.m. (p. 94) "Molecular Evolution and Studies on Methanobacterium formicicum"

J. Bush, R. Holmquist*, and T. Jukes

2:00 p.m. (p. 95) "Determining the Origin and Early Evolution of Living Organisms Based on Protein and Nucleic Acid Sequence Data"

M. O. Dayhoff*

2:20 p.m. (p. 96) "A Low Molecular Weight, Archaebacterial Adenosine Triphosphatase"

H. Kristjansson, C. Ponnamperuma, and L. Hochstein*

2:40 p.m. (p. 97) "A Yeast-Like First Eukaryote?"

H. S. Vishniac* and S. Baharaeen

3:00 p.m. Coffee

3:20 p.m. (p. 98) "Oxygen Requirements for Lipid Synthesis in Microorganisms"

L. Jahnke*, C. Volkmann, and H. P. Klein

3:40 p.m. (p. 99) "Primary and Secondary Energy Conversion in Halobacterium Membranes"

J. K. Lanyi* and B. Schobert

4:00 p.m. (p. 100) "Light Energy Conversion in Halobacteria"

R. A. Bogomolni* and W. Stoeckenius

4:20 p.m. (p. 101) "The Cryptoendolithic Microbial Community: A 'Closed' Ecosystem in Nature"

E. I. Friedmann*, R. O. Friedmann, L. Kappen, C. C. McKay, and J. R. Vestal

4:40 p.m. Adjourn

SESSION SUMMARIES

Session I: Extraterrestrial Chemistry

Chairman - Sherwood Chang

Papers delivered in the session on "Extraterrestrial Chemistry" addressed diverse aspects of the chemistry of the biogenic elements (H, C, N, O, P, S) that are related to interstellar clouds, the solar nebula, meteorites (and their parent bodies), Jupiter, and Saturn's satellite, Titan. Organic matter is known or inferred to exist in all these extraterrestrial environments. Attempts to elucidate its origins therein contribute to a general understanding of the processes involved in the chemical evolution of the solar system and the bodies within it.

It is appropriate to view the first four papers from the perspective that the organic matter observed in primitive solar system objects (like meteorites) may have components produced in interstellar clouds, the solar nebula, the parent body itself, and terrestrial environments. One major challenge is to sort out and identify these contributions.

DeFrees, McLean, and Loew have carried out quantum mechanical calculations to determine the geometries of HCCOH, HOCN, $HCNH^+$, and $HOCO^+$, which are molecules predicted by ion-molecule reaction schemes to occur in interstellar clouds. The frequencies of rotational transitions calculated from the geometries serve as the bases for microwave searches for these species. It is noteworthy that $HCNH^+$ is a key intermediate in the schemes for synthesis of HCN and other interstellar nitriles, and $HOCO^+$ may be a precursor for interstellar CO_2, whose geometry precludes microwave identification.

Chang, Gupta, Lawless, Shipp, and Wydeven reported that the results of plasma discharge reactions in H_2-CH_4 mixtures designed to simulate reactions that may have occurred in the solar nebula and contributed to the organic com-

pounds in meteorites. They found that unstable intermediates formed at 115°K survived and continued to generate additional hydrocarbon products at room temperature. This observation suggested that reactive interstellar species condensed on grains during the low temperature (≈20°K) isothermal stage of protostellar cloud collapse may have contributed to the chemistry of the solar nebula subsequently at higher temperatures. They also reported that synthesis of acetylenic compounds and preferential incorporation of ^{12}C relative to ^{13}C into products were favored by high abundances of H_2.

Cronin, Yuen, Pizzarello, and Frye used solid state ^{13}C-NMR spectroscopy to show that the acid-insoluble carbon-rich matter composing the bulk of the carbon in carbonaceous meteorites may exist in two forms, at least. The Orgueil (CI), Murchison (CM), and Allende (CV3) meteorites contained a common component with a dehydrogenated, polycyclic aromatic network as a basic structural feature. Orgueil and Murchison contained an additional component having hydrogen-containing aliphatic and aromatic-olefinic structures. The origins of these major carbon-bearing phases remain obscure, however.

Ogino and Nagy summarized a variety of control experiments carried out on a mixture of amino acids as a guide to determining their behavior and recovery during extraction from Murchison meteorite. Although these experiments were intended to place bounds on the contribution of terrestrial analytical procedures to the recently reported L-enantiometric excesses in Murchison amino acids, no firm conclusion regarding the origin of the excesses was drawn.

The next four papers dealt with the chemistry of the Outer Planets, where reactions are now occurring that may have taken place during their earliest history. This possibility had led to the speculation that the chemistry of Titan provides a model for that of a hypothetical primitive Earth endowed with

a H_2-CH_4-N_2 atmosphere.

Scattergood, Aronowitz, Flores, and Chang presented a quantitative assessment of the efficiency with which kinetically hot hydrogen atoms, produced by ammonia photolyses in the presence of large excesses of H_2, can abstract a hydrogen atom from CH_4, thereby producing a methyl radical. Their results now provide a basis for determining the extent to which hot hydrogen atom reactions can occur in hydrogen-rich as well as hydrogen-poor planetary atmospheres. In principle, these reactions can lead to organic synthesis in regions where the direct photolysis of methane cannot take place.

Ferris, Bossard, and Benson have elucidated the photochemistry of phosphine in the context of Jupiter's atmosphere. Their experiments show that diphosphine (P_2H_4) is the initial photoproduct in the photolysis of either PH_3 or NH_3-PH_3 mixtures. Apparently, diphosphine synthesis is independent of temperature above 175°K and uninfluenced by the presence of H_2 and N_2. These results serve as the basis for Ferris et al.'s postulation that the aerosols observed above Jupiter's NH_3 clouds may be composed of diphosphine.

Yung, Allen, Pinto, and Gardner described their investigations of the reactions in Titan's atmosphere initiated by ultraviolet light and high-energy particle bombardment. Their approach centered on a one-dimensional computational model which took into account exospheric hydrogen escape, secondary methane photolysis, synthesis of higher hydrocarbons, production of aerosols, and coupling of the chemistries of C, N, H, O-bearing species. The results of the model calculations predicted molecular abundances of atmospheric species in accord with those revealed by Voyager observations. They also added credence to the often-expressed view that large amounts of organic compounds should be condensed on Titan's surface.

Sagan and Khare pointed out that solid products, dubbed "tholins,"

produced by exposure of CH_4 and N_2 to high-frequency electric discharge, are endowed with physical properties consistent with those of Titan's cloud components. Thus tholin particle size, refractive indices, and spectral reflectivity in the near UV and infrared wavelengths longward of 6 μm were judged to be consistent with Titan observations. Based on their chemical and spectroscopic characterization of the artificial tholins, Sagan and Khare inferred that Titan's clouds are composed, in part, at least, of organic heteropolymers containing polynitrile and hydrocarbon functional groups.

Session II: Primitive Earth

Chairman - James Lawless

This session dealt with the processes that occurred on the putative primitive Earth, from the photochemical behavior of atmospheric components to the interaction of protobiological monomers with mineral surfaces.

The first paper, by Kasting, Zahnle, and Walker, discussed the numerical modeling of methane photochemistry in the anaerobic terrestrial atmosphere. The model considers the photochemical production (and loss) of more than 20 species and suggests that the concentration of CH_4 will depend strongly upon the amount of CO_2 present.

A second paper dealing with the photochemistry of the Earth's primitive atmosphere was presented by Bar-Nun and Chang. Gas mixtures containing H_2O and CO with various proportions of H_2, CO_2, and N_2 were experimentally subjected to UV light and to a simulated solar spectrum. The results suggested that even if the only form of carbon in the primordial atmosphere was CO, or CO and CO_2 (with no molecular hydrogen present), a variety of organic molecules could be produced by gas-phase photochemistry.

In a final paper considering the atmosphere of the primitive Earth, Miller and Schlesinger studied the synthesis of organic compounds in a spark discharge, using various mixtures of CH_4, CO, CO_2, H_2, H_2O, N_2, and NH_3. They showed that glycine is the major (only) amino acid produced from CO and CO_2 atmospheres, and, if the more complex amino acids are required, then their study shows a need for CH_4 in the primitive atmosphere.

In a series of studies by Folsome, aqueous suspensions of $CaCO_3$, formaldehyde, and hydrazine produced organic molecules when exposed to long wavelength UV light. He reported the presence of pyrimidines, amino acids,

deoxyribose, and organic microstructures. This is the first report of such species occurring from a single photochemical reaction.

Five papers dealt with the role of clays in the processes that could have led to the origin of life. Hartman discussed his new proposal in the area and summarized the role that iron-rich clays could have played in the fixation of CO_2 and N_2 into organic molecules. A paper by Bzik, Church, Lawless, Levy, Mazzurco, and Mortland discussed the ability of bentonite, homoionic in Zn, to concentrate nucleotides from dilute solution and selectively adsorb 5'AMP from a mixture which also contained the 2' and 3' isomers. A paper by Orenberg showed the effect of different metal ions on the adsorption of organic molecules onto homoionic clays. In general, it was observed that Trp was more strongly adsorbed than Phe on clays containing Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, or Zn^{2+}. White reported the effect of other organics (polyribonucleotides and peptides) on the catalysis of peptide formation on clay surfaces. He reported, for example, that 2 nmoles of His-His promotes the formation of 100 nmoles of additional glycine peptides and suggests that His-His acts as a catalyst in this process. In the final paper in the clay section, Coyne outlined the many-faceted role that clays could have played in the origin of life and reported on the blue to near-UV light released by the desolvation of a water-wet paste of kaolin. Studies are currently under way to correlate glycine oligomerization to this light emission.

A paper by Weber discussed possible prebiotic formation of phosphoanhydrides (such as ATP) using thioesters. He showed that thioesters which are energy rich are able to bring about anhydride formation and produce species such as pyrophosphate in the presence of hydroxyapatite, a phosphate mineral.

The final paper in this session was by Bonner and dealt with experiments on the origin and amplification of molecular chirality. Among the results

he reported was his recent finding that clays can protect amino acids against racemization.

Session III: Information Transfer

Chairman - Robert MacElroy

The problems of information transfer in primordial and early biotic systems range from fundamental questions about self-replication in nonbiotic systems through the evaluation of models for the origin and evolution of the genetic code.

At a most fundamental level are questions about the formation of the prebiological molecules that constitute the basic elements of a coding system. J. Oró discussed the role of cyanamide in condensing amino acids to oligopeptides, phosphatides to phospholipids, and nucleoside monophosphates to oligonucleotides. The fact that the yield of oligomers is increased in the presence of imidazole and arginine, he suggested, implies that a proton relay mechanism common to these compounds and to cyanamide, involving the (N=C-N-) group, may be operative.

S. Fox, with T. Nakashima and R.M. Syren, reported that thermal proteinoids containing sufficient basic amino acids act to catalyze the formation of peptide bonds between all types of amino acids in the presence of lysine-rich proteinoids. The sequence composition of the product (the proportion of gly and phe incorporated into phe-gly vs. gly-phe) is influenced by the presence of polynucleotides and polynucleotide-proteinoid. He suggested that a variant of this system that catalyzes the formation of polynucleotides may be an example of a reverse translation process.

A different approach to the formation of specific peptides has been taken by F. Eirich and M. Paecht-Horowitz, who reported on the role of clays in oligomer synthesis. They described the condensation of activated amino acids on clay surfaces and reported adsorption isotherms of amino acids and nucleotides. They also reported the effects on adsorption of preadsorbed

peptides, and of coadsorption of bases and nucleotides. They anticipate that their studies will illuminate the interactions on clay surfaces that lead to specific condensation products.

The transfer of information in the form of sequence-specific templating in the absence of enzymes has been approached experimentally by L. Orgel. Orgel, with T. Inoue and H. Fakhrai, reported further studies on an RNA polymerase model in which polycytidylic acid, acting as a template, is capable of generating a variety of polyguanidilic acid polymers, up to a length of 40 nucleotides with high fidelity. These studies have been extended to include the synthesis of mixed oligomers containing an excess of G directed by an oligomer containing an excess of C. Bases whose complements were absent from the template were not incorporated into the product oligomers.

The molecular basis of the function of Orgel's model has been examined using theoretical model approaches. R. Rein, with T. Kieber-Emmons, reported on an exploration of why polypyrimidines are effective templates for polynucleotide synthesis, while polypurines are not. Their results suggest that template efficiency is the consequence of a subtle interplay between conformational stabilities and helix compatibilities. By calculating binding isotherms for incoming nucleotides and the template polynucleotide strand, they were able to calculate the probabilities of chain elongation, thus providing an explanation for the sequence length distribution that is experimentally observed by Orgel and co-workers. Rein also described recent work on the interaction of specific peptides with nucleotide sequences (the lac system).

A major conundrum in studies of the origin of life is the relationship between the genetic code (a sequence of nucleotides) and the amino acids that the code specifies. Two papers addressed this problem. The first,

presented by M. Hobish, with C. Ponnamperuma and B. Cherayil, described NMR studies of interactions between nucleic acids and proteins. The results presented suggest that Mg ions affect the protons of 5'AMP interacting with phenylalanine methyl ester, causing a downfield shift in ring proton signal, and that the amino acid binds more strongly to 5'AMP (an anticodon monomer) than to 5'UMP (a codon monomer).

A very similar observation was made by J. Lacey, who reported binding constants of phenylalanine to AMP, GMP, CMP, and UMP of 6.6, 3.5, 2.1, and 1.1 M-1, respectively. Lacey extrapolated from these observations of affinity to suggest that they may provide the reason that the only anticodons of phenylalanine contain AAPu (3'>5'). He suggests that the reaction rates of hydrophobic amino acids with ATP are correlated with the affinities of these amino acids (phe, leu, ile, val, met) for ATP, and that a general principle can be postulated: that the rates of various chemical reactions between amino acids and nucleotides are a function of the affinity between the reacting species. An extension of this principle is that the genetic code arose as a consequence of selective affinities between amino acids and their anticodonic nucleotides.

Affinities and interactions between molecules are highly dependent upon the solvent in which they occur. A. Pohorille, with S.K. Burt and R. MacElroy, reported on model studies of solvent interaction with nucleic acid bases. The approach used was Monte Carlo simulation of solvent-solute geometries, which allows the calculation of system geometry and energy at equilibrium. The results were used to explain experimental observations that, in hydrophobic environments (using nonpolar solvents) an A-U (hydrogen bonded) pair is favored over an A/U (stacked) pair by 8 kcal/mole, while in a polar solvent (water) A-U is favored. By extension, such data can be used to explain that

phenomena such as nucleic acid stability are not due to hydrogen bonding but rather to an effect of the solvent.

Session IV: Solar System Exploration

Chairman - Glenn Carle

The session on Solar System Exploration was devoted to reports on current research studies in analytical concepts of gas chromatography. These studies were focused on application of the techniques to current and future opportunities to conduct analyses of extraterrestrial samples, where data would be acquired specifically to support exobiology science goals and objectives. Examples of candidate environments suggested in this session's reports included interplanetary dust or "Brownlee particles," outer planets and their moons, Mars, comets, and asteroids. The emphasis was placed on volatile compounds of the biogenic elements which might be found in the atmospheres or solid materials of these bodies.

Current state-of-the-art flight instruments, for example, Pioneer Venus Gas Chromatograph, which have been used in the past to make these measurements, have sensitivity limits of about 1 ppm for these chemical species. Further, no flight instrumentation is currently available to analyze volatiles included in solid phase materials. The reports at this session made it clear that the state-of-the-art has been advanced sufficiently so that these limitations, particularly sensitivity, will not apply to future flight instruments.

Fritz Woeller reported on his work with miniature metastable ionization detectors. He has developed a gas chromatograph detector which weighs approximately 1 gram and which universally detects down to 1 ppb levels of gaseous components in model planetary atmospheres. He showed comparison sensitivity data with current mass spectrometers, demonstrating that his detector has equal or better sensitivity. This detector does, however, require columns that are unusually stable and free from bleed, such as porous polymers and molecular sieves.

New types of column materials are now being prepared that are compatible with his detector and will expand its application to other than fixed gases. Glenn Pollock reported on reacted-in-place phases, such as substituted urethanes, which are bound directly to porous silica. Using these phases, he has produced miniature columns (1 mm I.D. x 75 cm long) which separate most low molecular weight hydrocarbons at room temperature in less than 3 minutes. These columns are fully compatible with the metastable ionization detector and are usable in quantitative analysis down to a few ppb.

Application of the new detector and column technologies to prototype instruments which would be useful in making flight measurements specific to exobiology goals has also progressed. Bonnie O'Hara reported on her instrumentation work in which she combined the metastable ionization detector with flight-type columns to study the volatiles that might be evolved from "Brownlee particles." Using Murray meteorite as a source of model particles, she was able to demonstrate the ability to analyze thermally evolved volatiles at the 100 ppm level in single 10 μm-sized particles. She plans to analyze "Brownlee particles" and report findings as samples become available in the laboratory.

The last report of the session was made by José Valentin on multiplex gas chromatography as an entirely new technique for analysis of planetary atmospheres. In this technique, many samples are rapidly admitted to a column without regard to elution time, followed by detection in the conventional manner. The signal is then subjected to mathematical deconvolution using, for example, Fourier transforms. He was able to demonstrate the usefulness of the technique in analyzing complex mixtures while producing an effective increase in sensitivity of 100-fold, that is, 100 ppb sensitivity using a commercial thermal conductivity detector.

Session V: Planetary Protection

Chairman - Donald DeVincenzi

The proposed new U.S. Planetary Protection Policy was presented in this session. This simplified and less stringent new policy proposes: deemphasizing the use of mathematical models and quantitative analyses; establishing requirements for target planet/mission type (i.e., orbiter, lander, etc.) combinations; considering sample return missions a separate category; simplifying documentation; and imposing implementing procedures (i.e., trajectory biasing, cleanroom assembly, spacecraft sterilization, etc.) by exception if the planet/mission combination warrants such controls.

Session VI: Future Directions

Chairman - John Billingham

The session on Future Directions began with a review by John A. Wood of a recent scientific workshop which examined the major scientific questions and research opportunities pertaining to the cosmic history of the biogenic elements (C, H, O, N, P, S) and their compounds. Most exobiological research in the past has begun with the evolution of organic molecules on the Earth, but the raw materials for those molecules have a long and complex preplanetary history. Wood summarized some of the findings of the group, which dealt with stellar nucleosynthesis, supernovae, stellar winds, the interaction of gas and dust in the interstellar medium with all types of radiation, gravitational collapses of interstellar matter, solar nebulae, the aggregation of planetesimals, and today's partial remnants of those early processes, the comets and meteorites of the solar system.

Mitchell Hobish next reviewed the recent discoveries of the deep sea hydrothermal vents in an ocean ridge near the Galapagos Islands. The chemistry, biology, and geology of these vents were the subject of a recent conference on the subject, organized by the University of Maryland. Hot water, laden with a wide variety of chemical species, pours out from the vents at temperatures which may reach over 300°C. Immediately around the vents is a complex and unusual ecosystem of microorganisms, shrimps, crabs, and strange large worms with no digestive system, all in total darkness. It is thought that the energy source for maintaining the system is chemoautotrophic, possibly sulfur bacteria. Hobish raised the question of whether the deep sea vents are an opportunity for investigating the concept of neoabiogenesis, as opposed to the conventional wisdom that once life is firmly established

on a planet it will prevent any later repetition of the origin of life process.

David Raup next summarized a series of three NASA interdisciplinary science workshops on the evolution of complex life (i.e., beyond the Precambrian Era). The group developed many research topics that need to be addressed on the relationship of astrophysical or solar system events to the evolution of complex life, on Earth or elsewhere. Raup showed an interesting curve depicting the progressive increase in the number of species during the Phanerozoic, punctuated by several major declines whose cause is still not completely understood (although the asteroid impact theory of Alvarez et al. has suggested one possible explanation). The central question is whether such extinctions accelerate, retard, or have no real influence on the long-term evolution of complexity, to which there does seem to be a trend. (It is of interest to note that all these considerations apply to Precambrian biology as well.)

John Oró next gave a talk on the role of exobiological science in the future of solar system exploration, as studied by another series of NASA science workshops held over the past year. The participants identified three major questions to be addressed: (1) What can the study of extraterrestrial organic chemistry tell us about the prebiological chemical era on Earth and elsewhere? (2) How did the formation and earliest history of the Earth set the stage for chemical and early biological evolution? (3) Once life has emerged, what is the impact of the evolution of life on the Earth's planetary evolution? The primary targets identified for solar system exploration, to help answer some of these questions, are: (1) small primitive bodies, comets, asteroids, meteorites, and interplanetary dust; (2) giant planets and their satellites, with special emphasis on Titan and Europa; and (3) terrestrial planets and their satellites, essentially Mars, Phobos, Deimos,

Venus, and the Moon.

The final paper was given by Frank Drake, who discussed the status of research on the Search for Extraterrestrial Intelligence (SETI). Detailed studies of the best way to carry out the search for extraterrestrial life have reconfirmed the idea that the most promising approach to the detection of other civilizations is to search for radio transmissions over a large part of the microwave spectrum, using fine resolution and examining millions of separate channels simultaneously. Such a "multichannel spectrum analyzer" would be used with existing large radio telescopes to look specifically at good target stars and also to carry out a sky survey to make sure that some unexpectedly strong signal is not being missed. Drake made some comments about searches elsewhere, particularly in the Soviet Union, where a number of large SETI programs are under way. He concluded with two fundamental points: (1) that the current approach is very conservative; it does not demand a science and technology on the part of the other civilization that is beyond our own; and (2) that the only sensible way to proceed is to carry out a search. It is probably the only way to achieve a detection in the near future, and hence to resolve the usual debates about probabilities for the existence of extraterrestrial life.

Session VII: Geological Record

Chairman - David Des Marais

This session examined the evidence for biological evolution as it is recorded in ancient rocks. The speakers discussed not only fossil studies but also the preservation of biochemical fossils, the evidence for ancient climates, and the evolution of volatile element chemistry on Earth.

Paul Abell presented chemical analyses of stromatolites in the Cheshire and Manjeri formations (2.7 b.y. old) of Zimbabwe. Abell, McClory, Nisbet, and Martin had noted that the primary sedimentary structures of these rocks were exceptionally well-preserved, and their carbonates were therefore well suited for the examination of Fe, Mg, Mn, Sr, and Rb abundances, as well as $\delta^{18}O$ and $\delta^{13}C$. The authors noted a cyclic variation in the mineralogy of the stromatolitic layers but were unable to find any correlative cyclic variations in the above chemical and isotopic parameters. The $\delta^{18}O$ in the carbonates ranges from -9 to -13; the $\delta^{13}C$ of the carbonate and organic matter ranges from -0.5 to +0.4 and from -30.2 to -34.7, respectively.

David Des Marais showed that the $\delta^{13}C$ of the carbon indigenous to mid-oceanic basaltic glasses is very close to -6 in samples from the Mid-Atlantic Ridge, the East Pacific Rise, and Hawaii. This value is very similar to the one obtained by mass averaging all the carbon in sediments. Such similarity indicates that the average carbon isotopic composition of the Earth's sedimentary reservoir has been remarkably constant over geologic time. Des Marais also presented evidence, from a collaboration with A. Truesdell, that most, if not all, of the hydrocarbons produced from continental geothermal systems derive from thermal decomposition of organic matter in the subsurface.

Kim Wedeking discussed his new procedure, developed with J.M. Hayes, for

$\delta^{18}O$ analysis of recent and ancient organic matter. The Indiana group has analyzed recent material from Antarctica, from a Florida lake, and from the ocean sediments of Tanner Basin (California) and Walvis Bay (SW Africa). They notice a good correlation between the $\delta^{18}O$ of the organic matter and the $\delta^{18}O$ of the environmental water. Examination of organic matter with depth in the Green River and Paris Basins reveals that $\delta^{18}O$ varies with the hydrogen content.

I.R. Kaplan reviewed his laboratory's recent findings concerning the diagenesis of organic matter. He first summarized the changes observed in elemental abundances, color, and chemical structure of the kerogen and its products. He then discussed his recent observations that clays such as kaolinite, illite, and montmorillonite can strongly influence both the relative production rates of methane and carbon dioxide and also the stable carbon isotopic composition of these diagenetic products.

G.G. Smith discussed the processes that influence amino acid racemization. He investigated how moisture increases the rate of racemization in a fossil hominid skull from La Caune Cave, France. He also studied the effects of metal complexation upon racemization using different cations (Co, Ni, Pd) and complex configurations (cis versus trans isomers). The racemization rates were highest for cobalt and palladium complexes, intermediate for free amino acids, and lowest for nickel complexes.

S. Golubic related details of his and S. Campbell's discovery of microbial endolith borings in the Eleonore Bay Formation (0.57 to 0.7 b.y. old), eastern Greenland. He discussed the structural details of these borings and how they are identified as being indigenous primary structures. He also presented observations from the Shark Bay stromatolites and discussed their significance regarding the destruction of potential stromatolites during the

Precambrian.

A.L. Burlingame summarized the history and significance of organic molecules which can be preserved in rocks to become biological markers ("biomarkers") of past life. His analyses of the Solar Lake (Sinai) microbial mat indicated how the mat can serve as a model for the synthesis and preservation of biomarkers in the natural environment. His pyrolysis GC-MS data illustrate that the cyanobacterial sheath material persists with depth in the mat whereas the abundances of the fatty acids, isoprenoids, and low molecular weight acids are substantially modified and removed.

F. Asaro, speaking for the L.W. Alvarez, W. Alvarez, and H. Michel group, discussed recently obtained chemical evidence for relationships between terrestrial asteroid impacts and biological extinctions. He reviewed the group's evidence for anomalously high Ir contents in samples obtained worldwide from the Cretaceous-Tertiary geologic time boundary. The elements platinum and gold are also anomalously high in these samples, as might be expected from the impact of a carbonaceous chondrite meteorite. This group is searching for elemental anomalies in rocks from other extinction episodes. They have found no anomalies at the Permo-Triassic time boundary; but may have identified an Ir anomaly at the Eocene-Oligocene boundary.

Session VIII: Early Biological Evolution

Chairman - Lawrence Hochstein

The 10 papers comprising this session covered three seemingly disparate topics: the phylogeny of microorganisms, putative models of early metabolic processes, and ecological models of primitive life. The unifying theme connecting these topics was the notion that contemporary organisms represent a fossil record within which resides evidence of the origin(s) and evolution of life.

The paper by Fox and Woese summarized their studies using 16S and 5S rRNAs. The data obtained with the shorter ribosomal RNA confirmed the earlier proposition that the Archaebacteria represent a collection of organisms so unique that their separation from other prokaryotes can be warranted. The results also suggested that anaerobic organisms preceded aerobic ones and that the photosynthetic genotype was an ancient one.

Bush, Holmquist, and Jukes described their test of the archaebacterial hypothesis by examining the aminoacyl tRNA synthetases from Methanobacterium formicicum. They proposed to establish a methanogen gene pool in an Escherichia coli host and to clone the appropriate aminoacyl transferase gene for sequence analysis and comparative acylation studies of tRNA from E. coli.

Dayhoff described phylogenetic trees constructed utilizing a variety of evolutionary probes. The resulting schemes provided a horizontal phylogenetic picture with much internal consistency and in good agreement with relationships suggested by others. 5S rRNA sequences were found to be consistent with the endosymbiotic hypothesis and indicated that the chloroplasts of higher plants were derived from Anacystis and Prochloron-like organisms, that mitochondria arose from a purple sulfur-like bacterium, and that the cytoplasmic constituents had their origins from an archaebacterial line re-

lated to Thermoplasma acidophilum or Sulfolobulus acidocaldarius.

The phylogeny of a variety of yeasts obtained from the dry valleys of the Antarctic was described by Vishniac and Baharaeen via a hybridization technique using 25S rRNA which they have developed.

Bogomolni and Stoeckenius described their studies with bacteriorhodopsin, which functions as a light-transducing proton pump. A variety of techniques have allowed them to define the photochemical cycle and the nature of the chromophore-binding site, and to identify a tyrosine moiety as being involved in the proton cycle. Lanyi and Schobert reported on a photochemical pigment, halorhodopsin, which at one time was thought to be a sodium pump. The evidence now indicates that this pigment functions as a chloride pump. Halorhodopsin in conjunction with a proton pump (bacteriorhodopsin) and a sodium/proton antiporter establish the sodium/potassium gradients characteristic of extreme halophiles while maintaining constant cell volume. Both papers made a strong case for using the light-transducing pigments of the Halobacteria as models of primitive energy transduction.

The presentation by Kristjansson, Ponnamperuma, and Hochstein dealt with the energy-transducing ATP-ase from Halobacterium saccharovorum. They pointed out that the notion of the ubiquitous distribution of the ATP-ases, which suggests that they arose early during evolution, was inconsistent with their complexity. A search for a simpler enzyme in the halobacter resulted in the characterization of an F_1 subunit with an unusually low molecular weight. The possibility that the halobacter group may provide a fertile arena within which to investigate the evolution of cellular processes should not be overlooked.

The studies of Jahnke, Volkmann, and Klein on the levels of oxygen necessary to sustain aerobic reactions involved in lipid metabolism in the

eukaryote Saccharomyces cerevisiae confirm their earlier observations that the levels of oxygen required are consistent with the levels that might have been present during the early transitions from an anaerobic to an aerobic atmosphere. These observations imply that eukaryotes could have arisen far earlier than previously thought.

Margulis and Stolz described their studies of the microbial mats in a saline laguna in Baja California. The possibility that these mats represent models of the creatures that gave rise to the Precambrian stromatolites was suggested. Friedmann and his coworkers described their recent work on Antarctic organisms inhabiting rocks. This endolithic environment consists of primary producers, consumers, and decomposers. The authors suggest that a study of such ecosystems may provide a clue to how early life was established on the primitive Earth.

The overall impression of this session was that extant organisms possess a tremendous storehouse of information from which the early origin(s) and evolution of life may be deduced.

SESSION I

EXTRATERRESTRIAL CHEMISTRY

Accurate Theoretical Predictions of the Rotational Constants of Candidate Interstellar Molecules

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In current theories, our solar system was formed 5 billion years ago by the gravitational collapse of a large cloud of dust and gas, the solar nebula. We have, of course, no direct evidence to support this idea. Indirect evidence lies in the nearby heavens where newly formed stars, and by implication solar systems, are observed to be imbedded in clouds of interstellar matter. An important question is what are these clouds of dust and gas made of? Any model for the formation of the earth and for the evolution of life upon its surface must be consistent not only with extrapolations of current conditions back into time but also with extrapolations made forward in time starting with the interstellar building blocks from which the sun, the planets, and other bodies in the solar system are thought to have formed. While we can't study the solar nebula, we can study other nebula believed to be possible star-precursors in the galaxy. An understanding of the composition and chemistry of galactic molecular clouds is necessary in order to understand the chemical evolution of solar system bodies which eventually led to the origin of life.

More than 50 molecules have been identified in interstellar space by, for most, comparing microwave emission frequencies obtained with radio telescopes to laboratory microwave spectra of known compounds. In several cases the laboratory studies were done after the astronomical observation had been made and a tentative identification made on theoretical grounds. Some molecules, ions and free radicals for example, are stable under interstellar conditions but unstable under terrestrial conditions and thus extraordinary means are needed to obtain laboratory spectra. Of the over 200 unidentified lines known to radio astronomers it is probable that some arise from such unstable molecules. Quantum mechanical calculations of a molecule's geometry can lead to a prediction of its microwave spectrum, which, of sufficient accuracy, can be used to assign unidentified radio lines. We have been able to obtain accuracies on the order of ±0.3% by the use of sophisticated molecular orbital theories and an empirical correction scheme. While this is not accurate enough to provide the definitive identification of new interstellar molecular species it can play an important role in guiding radio astronomical and laboratory searches as well as providing important corroborative evidence. We have made predictions of the microwave spectra of the candidate interstellar molecules $HCNH^+$, HCCOH, HOCN, and $HOCO^+$. $HOCO^+$ has tenatively been identified based, in part, upon the results of our calculations. Radio searches for $HCNH^+$ and additional searches for $HOCO^+$ will be carried out in early July using the computed spectra as basis.

PLASMA DISCHARGE: METEORITE ORGANICS MODEL

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In spite of the extensive efforts, the processes that led to the organics in meteorites remains poorly understood. Recent results on isotopic differences for C, H, and N between the solvent soluble and acid insoluble fractions of various meteorites clearly suggest a spatial and a temporal inhomogeneity in the formation and introduction of these materials into the parent bodies.

To gain insight into possible mechanisms responsible for these complex species in meteorites, we are currently exploring organic synthesis in a plasma discharge. Studies on the synthesis of organic molecules in heteorogeneous, non-equilibrium dynamic conditions (hydrogen rich, methane plasma discharge) have shown the production of linear and branched, saturated and unsaturated hydrocarbons. Trapping the products in liquid nitrogen and, subsequently, allowing them to warm to room temperature while monitoring their composition (1-24 hours) shows the formation of additional products indicating the presence of chemically reactive intermediates. The possible reaction mechanisms and ^{13}C isotopic data will be presented. The relationship of this work to other studies of laboratory simulated cosmochemical environments will be discussed.

^{13}C NMR SPECTROSCOPY OF THE INSOLUBLE CARBON OF CARBONACEOUS CHONDRITES

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A record of chemical evolution has been uniquely preserved in carbonaceous chondrites in the form of a diverse suite of indigenous organic compounds. Although many compounds common to terrestial life are found in these meteorites, the composite lacks the selectivity expected of biotic products. Thus meteorites appear to bear witness to an episode of organic chemical synthesis predating or occurring early in the history of the solar system.

The carbonaceous matter in these meteorites can be divided into soluble and insoluble fractions. Although the insoluble carbonaceous matter may account for from 70 to essentially 100 percent of the total carbon, the chemical structure of this material is not well understood. In order to better characterize this material, solid-state ^{13}C NMR techniques have been applied to the insoluble residue obtained after HF-HCl digestion of three carbonaceous chondrites. Cross polarization magic-angle spinning ^{13}C NMR spectra were obtained of the insoluble carbon of the Orgueil (CI), Murchison (CM2), and Allende (CV3) meteorites. The Murchison and Orgueil residues give spectra similar to terrestrial coals and oil shales with two major features attributed respectively to carbon in aliphatic (sp^3) and aromatic/olefinic (sp^2) structures. The spectrum of the Allende insoluble carbon does not show these features. Without cross polarization all three meteorite digests give spectra with a single feature at 150 ppm. These results are consistent with a dehydrogenated polycyclic aromatic network as a basic structural feature of the insoluble carbon of all three meteorites. The CI and CM2 meteorites have, in addition, structurally diverse, hydrogen-containing aliphatic and aromatic/olefinic structures.

BEHAVIOR AND RECOVERY OF SOME AMINO ACIDS FROM THE MURCHISON METEORITE: RESEARCH IN PROGRESS

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Detailed understanding of the nature of amino acids in carbonaceous chondrites, and their potential alterations during their extraction from these meteorites, probably will elucidate some of the more fundamental aspects of chemical evolution, with hope of shedding light on the evolution of life on Earth. The reason for this is that amino acids in carbonaceous chondrites may represent a relatively advanced stage in chemical evolution, unaltered by recycled biological overprints as one may envision for chemical processes on Earth. This chemical evolutionary significance is valid only if terrestrial contaminations can be subtracted from indigenous moieties, which, as is known, is a considerably difficult task.

The nature and the quantitative and qualitative recovery of amino acids from a stone of the Murchison meteorite is studied by a series of experiments in this laboratory. (1) A mixture of phenylalanine, tyrosine, methionine, glutamic acid, serine and isovaline were prepared and derivatized to N-PFP-, O-acetyl-(+)-2-butyl esters for gas chromatography. The major loss of these amino acids occurred during the 6N HCl hydrolysis and cation exchange steps; amino acid concentrations, and the volume of NH_4OH used to elute the amino acids from the cation exchange column affected the recovery. (2) The decomposition of serine obeyed reversible first order kinetics in H_2O with phosphate buffer, pH=6.9; (activation energy: 24.60 kcal/mole; frequency factor, ln A(yr^{-1}): 33.0) and in H_2O with admixed meteorite (10.60 kcal/mole; ln A (yr^{-1}): 19.4). In a similar kinetic experiment, designed to simulate initial terrestrial contamination and subsequent storage, serine in the absence of H_2O and in air (18.40 kcal/mole; ln A(yr^{-1}):26.7) showed that the extent of decomposition, under these conditions, at 25°C during 11 years is quite limited. (3) Notable quantities of alanine and α-amino-n-butyric acid were synthesized from serine and threonine, respectively, in the presence of H_2O and meteorite powder at 150°C. (4) L-aspartic acid became notably racemized when it was added to, and heated with, Murchison meteorite powder and H_2O at 110°C or 105°C for 20 hrs in an attempt to evaluate whether certain extraction procedures may racemize amino acids. The concentration of the added L-aspartic acid was in large excess compared to the indigenous meteorite aspartic acid. The meteorite sample to water ratios and probably also the ratios of L-aspartic acid to sample and water seem to affect the extent of racemization. 25 mg Meteorite powder heated with 0.05 ml H_2O at 105°C for 20 hrs indicated a pH of $\gtrsim$8.5. The value of $(D/L)_{t=20hrs} - (D/L)_{t=0}$ of L-aspartic acid heated in H_2O at 105°C was closely similar to the same value calculated from data reported in the literature from another laboratory, i.e. 0.0143 vs. 0.0142, respectively.

MARS' EARLY CLIMATE - A POSSIBLE HABITAT FOR TERRESTRIAL TYPE PRIMITIVE ORGANISMS

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Of all the other planets in the solar system, Mars is the most likely to have supported some form of life. While today Mars' atmosphere is tenuous and the surface is cold, dry and bombarded with lethal ultraviolet radiation, conditions may have been much different in the past. Recent estimates indicate that one to three bars of CO_2 may have been outgassed and could have resided in the atmosphere prior to being bound in the regolith. The many channels and valleys also provide ample evidence that water flowed on the surface and thus would have been present in the atmosphere certainly in larger concentrations than we find today.

Could these larger amounts of CO_2 have provided the necessary warming (greenhouse effect) to maintain temperatures above freezing over portions of the planet even though the solar constant was smaller? While modeling studies can never demonstrate that Mars at some time in the past contained terrestrial life forms, nevertheless if it can be shown that physical conditions on the planet yield climate spaces compatible with terrestrial organisms, then these studies would motivate and focus further planetary exploration which could help us to understand the evolution of life on our own planet.

The latitudinal distribution of surface temperature has been calculated from a simplified thermodynamic energy equation that includes radiation (solar and longwave), potential energy, sensible, latent, convective heat, and allowing for mean meridional and eddy transport. The major input parameters are obliquity, solar radiation, and atmospheric carbon dioxide.

For present-day Martian conditions (albedo, solar radiation and CO_2), the model calculation gives results that agree with measured values; the mean surface temperature is 218K and polar cap temperatures are within a few degrees of the condensation temperature. The atmosphere is not capable of supporting 1 bar of CO_2 alone. A large temperature increase does not occur when the CO_2 increases to 1 bar since even with present day CO_2 the major bands are nearly saturated. Polar temperatures are well below the CO_2 deposition temperature and even near the equator the temperature has not reached 273K. With a 25% reduction in solar radiation the polar and equatorial temperatures are 155K and 220K respectively.

The greenhouse effect due to different amounts of water vapor will be discussed as well as the ultraviolet radiation reaching the surface.

AN INVESTIGATION OF THE EFFECTS OF HOT ATOM CHEMISTRY OF MINOR CONSTITUENTS IN THE ATMOSPHERES OF JUPITER AND SATURN

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Studies of the atmospheres of the outer planets by both ground based telescopes and by space borne probes have shown these atmospheres to be complex mixtures of gases and aerosols. In addition to hydrogen, helium, methane and ammonia, all of which are expected to be present on the basis of thermodynamic cooling of the primordial solar nebula, ethane, acetylene and phosphine have been detected on Jupiter and Saturn. These molecules, along with the swirling colored clouds, are indicators of active disequilibrium processes (chemistry). In the upper atmospheres photolysis and particle bombardment of methane can account for the presence of ethane and acetylene. In the vicinity of the white ammonia cirrus clouds where phosphine exists, the methane is shielded from photolysis by the overlying atmosphere. Photolysis of ammonia yields only colorless hydrogen and nitrogen. Thus another process for the coupling of carbon with nitrogen or phosphorus to form organic molecules in this region is required. One possible pathway is provided by the production of methyl radicals from the reaction of hot hydrogen atoms (from photolysis of ammonia) with methane. These radicals can then react with each other and with methane and ammonia to form more complex organic compounds. Since planetary processes that prevailed soon after the origin of the solar system may be occurring now, knowledge of chemical processes operating in various planetary atmospheres should provide important data for correlating the relationship between chemical evolution and planetary evolution in the solar system.

For the study of hot hydrogen atom initiated synthesis of organic compounds in planetary atmospheres, a technique for the low level monitoring of the reaction of hot H with methane ($H^* + CH_4 \rightarrow CH_3 + H_2$) using CD_4 and analysis of the product HD by stable isotope mass spectrometry was developed. Using this method a suite of experiments on the 1849Å photolysis of mixtures of hydrogen, ammonia and deuterated methane (representing model Jovian atmospheres) were carried out. For three ratios of CD_4 / NH_3 of 10/4, 20/4 and 40/4 (in mm Hg) the hydrogen pressure was varied stepwise from 0 to 800 mmHg to study the effects of hydrogen on the process. Preliminary analysis of the experimental results indicates that although the efficiency of the hot atom abstraction process is low, ranging from 0.5 - 5% depending on the mixture composition, hot hydrogen atoms from the photolysis of ammonia can decompose co-existing methane in the presence of hydrogen Also the diminution of the yield of HD with added H_2 was less than expected based on thermalization of the hot H by 'elastic' collisions with H_2; thus hydrogen is not as effective as was believed. These results support the contention that hot H chemistry can occur in hydrogen-rich planetary atmospheres and can drive organic synthesis in regions where the direct photolysis of methane cannot occur.

PHOSPHINE PHOTOLYSIS. APPLICATIONS TO JOVIAN ATMOSPHERIC CHEMISTRY

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The discovery of phosphine (PH_3) in the atmospheres of Jupiter and Saturn prompted renewed interest in PH_3 photochemistry. It has been suggested that the color of the Great Red Spot on Jupiter is due to the rapid transport of PH_3 from lower atmospheric levels to the stratosphere where it is photochemically converted to red phosphorus by solar ultraviolet light. Since PH_3 is present above the cloud layers on both Jupiter and Saturn its photolysis to red phosphorus should be prevalent and not restricted to specific locales such as the Great Red Spot. Laboratory studies of PH_3 photochemistry were undertaken to provide a better experimental basis for these theories. This work will also provide guidance in the design of experiments for the Galileo probe of Jupiter as well as for ground based infrared studies which will investigate the molecular species present in the atmospheres of Jupiter and Saturn.

Photolysis of PH_3 with a 207 nm light source gives diphosphine (P_2H_4) as the initial photoproduct. It is formed in the gas phase by the combination of two PH_2 radicals with a diffusion-controlled rate constant (5.4×10 $M^{-1}s^{-1}$) which is comparable to that for the formation of N_2H_4 from NH_2. Neither N_2, SF_6 nor H_2 have a significant effect on the rate of formation of P_2H_4 from PH_3 or the rate of conversion of P_2H_4 to red phosphorus. Photolysis of PH_3-NH_3 mixtures results in the conversion of the PH_3 to P_2H_4 even though NH_3 is absorbing 90% of the light. This is due to the reaction of PH_3 with the radical species (NH_2 and H) formed by the photolysis of NH_3. P_2H_4 formation is independent of temperature above the melting point (174K). Its rate of formation does not change at temperatures below 174K but its stability increases below this temperature due to its condensation as a solid. We postulate that the aerosol layer above the NH_3 clouds (Axel or Danielson dust) may be due to P_2H_4 formed from PH_3 which condenses to a solid at the 110-150K temperatures present in the Jovian stratosphere. Initial quantum yields have been measured for the formation of P_2H_4 (0.80), H_2 (1.0), and phosphorus (0.04) and for the loss of PH_3 (1.78). A new mechanism is proposed for the photolysis of pure PH_3 and PH_3-NH_3 mixtures based on these data.

PHOTOCHEMISTRY OF METHANE, NITROGEN AND CARBON MONOXIDE ON TITAN - ABIOTIC SYNTHESIS OF ORGANIC COMPOUNDS

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The photochemistry of the major species containing carbon, hydrogen, nitrogen and oxygen in the atmosphere of Titan has been investigated using a one-dimensional model with realistic exospheric boundary conditions, vertical transport and heterogeneous processes at the tropopause. An extensive set of reactions has been compiled and critiqued. To estimate the rate coefficients of reactions which have not been measured we employ a number of innovative techniques such as Troe's semi-empirical theory for computing three-body recombination rate constants. Starting with CH_4, N_2 and CO, and invoking interaction with ultraviolet sunlight, energetic electrons (of magnetospheric origin), and cosmic rays, the model predicts correctly the concentrations of all other species, as observed by the Voyager IRIS and UVS instruments. The model is characterized by six simple concepts: (a) escape of hydrogen, (b) secondary photolysis of CH_4, (c) synthesis of higher hydrocarbons, (d) production of photochemical haze layers, (e) coupling between nitrogen and hydrocarbons and (f) coupling between oxygen and hydrocarbons. Our results suggest that photochemistry plays a major role in the present day climatology and past evolution of the satellite. Titan might have lost the equivalent of 10, 1 and 1 present atmospheres of CH_4, N_2 and CO respectively over geologic time. Most of the volatiles were photochemically converted into condensible organic compounds and deposited on the surface. The implications of abiotic organic synthesis on Titan for the origin of life on Earth are briefly discussed.

THE ORGANIC CLOUDS OF TITAN

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In the light of Voyager 1 Titan results, a mixture of 9% CH_4 and 91% N_2 was exposed for 10^7 secs at a total pressure of 73 mb to high frequency electrical discharge. The gas phase products include NH_3, HCN, $(CN)_2$ and other molecules. Solid phase products, here called tholins, appear as a thin red film which, under scanning electron microscopy, is found to be comprised of irregular micron and sub-micron sized particles, with a preponderance of particles exhibiting a radius $\simeq 0.3$ μm. The wavelength-dependent real part of their refractive indices $n=1.6 \pm 0.1$. These properties seem to be consistent with those deduced for the Titan aerosols from Earth-based observations (Rages and Pollack, Icarus 41, 119, 1980). Values of $n(\lambda)$ and $k(\lambda)$, and the uv, visible and ir reflectivities of these tholins have been measured, and compared with the CH_4/NH_3 and $CH_4/NH_3/H_2S$ tholins described earlier (Khare et al. Science 199, 1199, 1978; Sagan and Khare, Nature 277, 102; 292, 536, 1979). The spectral reflectivity of this tholin has been measured between 0.38 and 1.1 μm. The tholin absorbs strongly between 0.38 and 0.60 μm, and in this wavelength range follows, within the probable errors, the measured reflectance of Titan. At longer wavelengths, where the CH_4 Kuiper bands become prominent, the tholin, not masked by CH_4 absorption, continues to increase in reflectivity. We find that the infrared absoption spectra of tholins we have previously reported on can be explained by a weighted linear superposition of the absorptions by the most abundant organic functional groups appearing as GC/MS pyrolyzates. The infrared spectrum of the Titan tholin is similar, and suggests that this material is a complex heteropolymer which contains, among others, nitrile and hydrocarbon functional groups. The infrared reflection spectra of the Titan tholin longward of 6 μm and in the near ultraviolet are flat and approximately featureless, consistent with Titan observational results from the International Ultraviolet Explorer and from the Voyager IRIS experiments, respectively. The Titan tholin may include polynitriles with hydrocarbon functional groups. It seems likely that the Titan clouds are composed, at least in part, of organic molecules, as proposed some years ago (Sagan, Space Sci. Revs., 11, 73, 1971; Icarus 18, 649, 1973; Khare and Sagan, ibid 20, 311, 1973). From the direct photolysis of methane alone by ultraviolet light at wavelengths shortward of 1440 Å, the accumulation of organic tholins on the surface of Titan over geological time amounts to a surface layer tens of meters thick. Other energy sources serve to increase this number. At the 95°K surface temperature of Titan these organic heteropolymers will tend to be preserved for very long periods of time. It is therefore possible that the surface of Titan is a planet-scale repository of some of the early steps which led on Earth -- more than 4×10^9 years ago and in the presence of liquid water -- to the origin of life. It is also conceivable that the abundant water ice in the interior of Titan (deduced from the satellite's bulk density) is intermittently released in liquid form to the surface, and that subsequent aqueous tholin chemistry occurs even if episodically and on local scales.

SESSION II

PRIMITIVE EARTH

PHOTOCHEMISTRY OF METHANE IN THE EARTH'S EARLY ATMOSPHERE

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The photochemistry of methane in the primitive terrestrial atmosphere is potentially interesting in regards to both the origin and evolution of life. Methane has long been a favored starting point for the chemical evolution of life. If it were present in the primitive atmosphere, methane's photochemical byproducts, which can include formaldehyde, hydrogen cyanide, etc., would have formed ready source material for the subsequent biochemical evolution of amino acids, nucleic acids, and other basic building blocks of living matter.

Once life had formed, methane could easily have played a role in the co-evolution of life and the atmosphere. Methane would have been produced by the methanogens, an ancient class of anaerobic life that presumably were alive -- and possibly flourishing -- in the anaerobic biosphere that characterized the first 1.5 billion years of terrestrial life. A fraction of this methane would have polymerized into more complex hydrocarbons. Infrared absorption by methane and especially by other hydrocarbons may have supplemented the greenhouse warming due to CO_2 and H_2O, thus counteracting the cool sun and raising the possibility that the Gaia hypothesis may have applied to the anaerobic earth and its transition to aerobic conditions. (Speculation: the destruction of the methane greenhouse early in the Proterozoic may have triggered the Huronian glaciation.)

We present here a detailed series of one-dimensional numerical models for methane photochemistry in the anaerobic terrestrial atmosphere. The model solves the coupled equations of photochemical production (and loss) and diffusion for 22 chemical species, an additional 12 species are put in photochemical equilibrium. Steady state CH_4 mixing ratios of 10^{-6} to greater than 10^{-4} could have been maintained by a methane source of about 10^{11} molecules $cm^{-2}sec^{-1}$ (global average), which is comparable to the modern biogenic production rate, though a couple of orders of magnitude less than the modern abiogenic production rate. Thus, we find that methane-rich biogenic atmospheres are inherently plausible. In the absence of a source, methane would have disappeared in some 10^4 years in a series of chemical reactions initiated by reaction with either OH or O, being oxidized or being polymerized into more complex hydrocarbons. The source strength needed to maintain a steady CH_4 mixing ratio and the degree to which it would have polymerized depend strongly upon the amount of CO_2 present, while the dependence upon H_2 is much weaker. Our calculations also suggest that atmospheres rich in both CO_2 and CH_4 may be photochemically unstable with respect to conversion to CO.

PHOTOCHEMICAL REDUCTION OF CARBON MONOXIDE IN THE EARTH'S PRIMITIVE ATMOSPHERE

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The absence of a geological record makes a firm assessment of the atmospheric composition during Earth's first 0.8 billion years virtually impossible. Suppositions for the atmosphere range from H_2-rich, containing H_2-CH_4-NH_3-N_2-H_2O-H_2S, to H_2-depleted, containing CO-CO_2-N_2-H_2O-SO_2. Although organic syntheses in H_2-rich mixtures has been studied extensively, relatively little work has been reported on the CO-CO_2-N_2-H_2O system. Since solar radiation is the most abundant energy source in the atmosphere, photolytic investigations of the latter mixture are essential for an assessment of the full range of possibilities for the synthesis of organic matter on the primitive Earth. The photochemical experiments summarized below focused on the purely gas phase reactions of H_2O, CO, CO_2 and N_2; they were intended both to elucidate production mechanisms and to simulate reactions that could have occurred on the prebiotic Earth either above the cloud tops, at altitudes of about 10 km, where the abundance of water vapor is still considerable, or in an atmosphere containing few clouds.

Gas mixtures containing H_2O and CO with various proportions of H_2, CO_2, and N_2 were irradiated with 185 nm light or a simulated solar spectrum from which short wavelength UV was blocked by a filter cell containing O_2. Alchols, aldehydes, hydrocarbons, acetone and acetic acid were produced; no nitrogen-containing organic compounds were detectable. The initial step in the reactions involved photodissociation of H_2O molecules to yield hot H-atoms and hydroxyl radicals; the former reduced CO and recombined to H_2, while the latter oxidized CO to CO_2 and generated additional H-atoms. Changes in gas composition with irradiation time suggest that the organic products arose from a series of consecutive reactions in which CO was converted first to aldehydes and alcohols, which then were further hydrogenated to hydrocarbons. The overall apparent quantum yield for conversion of CO to organic carbon varied between 0.23 and 0.03 as a function of CO abundance. These results indicate that, even if the primordial atmosphere contained carbon only in the form of CO or a mixture of CO and CO_2, and no molecular hydrogen, a variety of organic compounds would have been produced by gas phase photochemical processes.

Upper and lower bounds can be crudely estimated for the "average" concentration of organic carbon in a hypothetical "global" ocean resulting from rain-out of products produced solely by photolysis of H_2O in the presence of CO. These calculations are made in the context of existing models for formation of the atmosphere and rely on estimates of primordial UV fluxes and terrestrial H and C inventories coupled with the apparent quantum yield for synthesis of organic C. For the case in which the total carbon inventory is released as CO over 10^8 years, in 10^6 years, the concentration organic C could have been as high as 0.02 M in a global ocean 30 m deep. For the case in which CO was released as a minor constituent and the atmospheric generation time was 5×10^8 years, the concentration would have been 0.0004 M. Gas phase photochemistry was certainly only one of the many possible sources of prebiotic organic matter. It is also unclear whether the types and amounts of organic compounds discussed above were necessary or sufficient for chemical evolution of organic matter to proceed beyond the monomer stage to attain higher levels of molecular organization. A satisfactory answer to this larger question awaits a more thorough accounting of the sources of simple organic compounds and the pathways for their conversion to more complex systems on the prebiotic Earth.

THE ATMOSPHERE OF THE PRIMITIVE EARTH AND THE PREBIOTIC SYNTHESIS OF ORGANIC COMPOUNDS

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There is considerable controversy concerning the composition of the earth's atmosphere at the time of synthesis of the organic compounds which organized into the first living organism. Compositions proposed range from strongly reducing atmospheres containing CH_4 to more oxidized atmospheres containing mainly CO_2 as the carbon source. There is also a controversy concerning the presence of NH_3 in the atmosphere and as a consequence NH_4^+ ion in the primitive ocean. Opinion varies from no NH_3 and NH_4^+ at all to partial pressures of 10^{-8} to 10^{-6} atm of NH_3 and 10^{-3} to 10^{-2} M NH_4^+ in the primitive ocean. It is generally agreed that O_2 was absent. There is no geological evidence about the composition of the atmosphere at 4.0 to 4.6×10^9 years ago. The oldest known rocks, the Isua formation of Greenland, dated at 3.8×10^9 years obviously cannot provide evidence for conditions on the earth 0.5×10^9 years before they were formed. Although a number of prebiotic synthesis experiments using CO or CO_2 instead of CH_4 as a carbon source have been reported, there has never been a systematic investigation of the comparative products and yields.

We have studied the prebiotic synthesis of organic compounds using a spark discharge as a source of energy. Methane mixtures contained $H_2 + CH_4 + H_2O + N_2 + NH_3$ with H_2/CH_4 ratios from 0 to 4 and $pNH_3 = 0.1$ mm. The yields of amino acids were approximately independent of the H_2/CH_4 ratio (1.5 to 4.7% yield based on the carbon), and a wide variety of amino acids were obtained. Mixtures of $H_2 + CO + H_2O + N_2 + NH_3$, $H_2 + CO + H_2O + N_2$, $H_2 + CO_2 + H_2O + N_2 + NH_3$, $H_2 + CO_2 + H_2O + N_2$, all gave about 2% yields of amino acids at H_2/CO and H_2CO_2 ratios of 2 to 4. For the H_2/CO and H_2/CO_2 ratios less than 1, the yields fall off drastically (as low as 10^{-3}%). Glycine is almost the only amino acid produced from CO and CO_2 atmospheres.

These results show that the maximum yield is about the same for the three carbon sources at high H_2/carbon ratios, but that CH_4 is superior at low H_2/carbon ratios. In addition, CH_4 gives a much greater variety of amino acids than either CO or CO_2. If it is assumed that the more complex amino acids were required for the origin of life, then these results indicate the need for CH_4 in the primitive atmosphere.

The hydrogen cyanide and formaldehyde yields parallel the amino acid yields; yields of HCN and of H_2CO as high as 10% based on the carbon were obtained in some experiments. NH_3 is also produced in experiments with no added NH_3 in yields as high at 4.6%. These results show that large amounts of NH_3 would have been synthesized on the primitive earth by electric discharges. The amount of ammonia formed by hydrolysis of the HCN may have exceeded that formed directly in the electric discharge.

Chemical Evolution and Model Photosynthetic Protocells

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Can biochemicals be synthesized under plausible primordial geochemical conditions? Current views of the primitive terrestrial environment suggest an atmosphere of nitrogen, water vapor and present-day abundances of carbon dioxide. This research asks whether organic compounds can be made under these anoxic conditions from simple precursors as CO_2, water and various nitrogen sources, using long wavelength ultraviolet energy. Implicit in this approach is the idea that primordial biochemistry centered about photosynthetic reactions mediated by phase-bounded systems.

We have shown several routes which lead to the synthesis of organic compounds under anoxic conditions. (1) Synthetic cell-sized organic microstructures effect the long-wavelength ultraviolet photosynthesis of formaldehyde, amino acids and other compounds from water, carbonate and various simple nitrogen sources (Nature 291: 482, 1981). Electrical discharges through nitrogen upon aqueous suspensions of calcium carbonate result in the formation of hydrazine, carbohydrazides and other organic products (Nature 294: 64, 1981.). These data show that the anoxic primordial atmosphere model is sufficient to account for the genesis of organic compounds during the origin of life. More recent data, summarized below, indicate that the anoxic photochemical model yields a wide variety of organic molecules of biochemical interest.

Recent findings: When aqueous suspensions of $CaCO_3$, ^{14}C-labeled formaldehyde, and hydrazine are exposed to long wavelength UV (254 nm) the following products are obtained: (1) free amino acids, (2) uracil and other dihydropyrimidines, (3) deoxyribose and other sugars, (4) organic microstructures, (5) other as yet unidentified organic products. Identification was effected by extensive thin layer chromatography, by gas chromatography/mass spectrometry, and by liquid chromatography (the 14-C label of the input formaldehyde was recovered in these products). This is the first instance in which pyrimidines, deoxyribose, amino acids, and organic structures have simultaneously been recovered in good yields from a single photochemical reaction.

CLAYS AND THE ORIGIN OF LIFE

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Clays are made up of various ions imbedded in a layered silicate structure. The ions involved are mainly aluminium, iron and magnesium. Clays are formed when water caused the chemical weathering of rocks. The concentration of ions in clays (e.g., iron, magnesium) is extremely variable and thus clays can be considered solid solutions. In 1965, Cairns-Smith proposed that the original genes were clays. The distribution of ions played the role of bases in DNA. Recently, A. Weiss has replicated clays in the laboratory for twenty-two generations. We have proposed that it was on the surface of replicating iron-rich clays that carbon dioxide and nitrogen would be fixed into organic molecules.

The synthesis (low temperature and pressure) of iron-rich clays are being carried out. The syntheses of glauconite and nontronite has been successful. The interaction of coenzymes with homoionic clays has been studied, in particular the interaction of pyridoxal phosphate and Cu montmorillonite. An activation of the coenzyme by the clay was demonstrated. The interaction of phospholipids and Ca^{++} montmorillonite led to the formation of a lipid bilayer between the clay particles. We are now studying the phase transitions of the lipid bilayer by physical and chemical means. The reduction of carbon dioxide to formaldehyde in the presence of Fe^{++} ion and light has been demonstrated by Getoff, we have looked at the inverse process which involves the oxidation of sugars by Fe^{++} ion and light. This implies that the iron cycle would be coupled to the carbon cycle, very early in chemical evolution. We are thus looking for a photosynthetic organism which would use the electrons from a ferrous ion to reduce carbon dioxide. Finally we are modeling the synthesis of polar organics on carbonaceous chondrites. Our model suggests that γ radiation supplied by A ℓ_{26} reduced the carbon dioxide and nitrogen on the surface of the iron-rich clays.

THE ADSORPTION OF BIOMONOMERS ONTO HOMOIONIC CLAYS

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In previous studies, we have shown that Zn-bentonite strongly adsorbed the purine nucleotides, and specifically adsorbed 5'-AMP from a mixture containing 5', 3', and 2'-AMP. This behavior is not predicted from homogeneous solution behavior and will be discussed. Excess NaCl in the solution does not significantly change the adsorptive behavior of the nucleotides. The presence of zinc or magnesium in solution will enhance the adsorptive behavior of ATP onto Zn-bentonite, while magnesium in solution will not effect the limited adsorption of ATP onto Mg-bentonite. Smectites with polyvalent cations on the exchange sites readily adsorb riboflavin from aqueous solution. Finally, Ca-vermicullite showed no adsorption, suggesting that this mineral does not swell sufficiently to permit intercalation. Temperature appears to have a significant impact on the adsorption of amino acids (alanine, β-alanine, δ-aminobutyric acid) onto Cu-bentonite. Implications for our studies in chemical evolution and the origins of life will be discussed.

CATALYSIS OF PEPTIDE FORMATION ON CLAY SURFACES BY POLYRIBONUCLEOTIDES AND BY SHORT PEPTIDES

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The origin of genetic processes and the appearance of collections of molecules which could reproduce themselves are the least understood aspect of the origin of life on the primitive Earth. The objective of this research is to demonstrate that simple molecules could carry out catalysis and templating during peptide bond formation, which might lead to a crude but spontaneous laboratory model for primitive translation.

Glycine reacts to form peptides on the surface of clays which are alternately wetted and dried. We have shown that the mechanism of this reaction involves the formation of an activated acyl silicate, which is analogous to the acyl phosphates (amino acid adenylates) which provide the energy for protein synthesis in living cells. The reaction of glycine on clays is catalyzed to a remarkable extent by histidyl-histidine and other peptides. Only 2 nmol of His-His promotes the formation of 100 nmol of additional glycine peptides. This suggests that His-His is a model for a primitive enzyme, able to repeatedly catalyze the synthesis rather than degradation of biologically important molecules. Polyribonucleotides also catalyze the reaction of glycine on clay surfaces, and we have recently demonstrated that 10 nmol of Poly G promote the formation of 40 nmol of additional peptide, which is the first time that greater than stoichiometric results have been obtained. For this and several other reasons, we believe that a simple template is involved in this reaction. We are trying to demonstrate directly that templating is involved, and that polyribonucleotides can select certain amino acids preferentially from a mixture, but so far we have not succeeded. Theoretical work by the author suggests that peptide catalysts might enhance the selectivity of a template, so our eventual goal is to demonstrate whether this effect can lead to a significant translation effect.

SOLVATION/DESOLVATION INDUCED LUMINESCENCE IN KAOLIN - INDICATOR OF SURFACE REACTIVITY?

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Electronic excitation produced by diverse energy sources can be similarly stored in catalytic minerals as separated trapped charges. My research of the last several years has produced an elaborate web of circumstantial evidence which links this energy to the chemical reactivity of adsorbed organic molecules important to the origin of life. If it can be shown irrefutably that a genuine link exists between energization of a mineral catalyst and reactivity of adsorbed organics, then it can be argued that chemical evolution would have proceeded much more rapidly than our laboratory simulations of it. I am exploring this link by correlating mineral luminescences, ESR and chemical reactivity as a function of pre-heating and pre gamma irradiation of the mineral catalyst.

Investigations of glycine oligomerization on pretreated kaolin using a wet/cold hot/dry cycled reaction protocol have shown that the yield of peptide bonds can be enhanced by thermal and gamma-irradiative pretreatment of the kaolin. TL efficiency also varies as a function of these pretreatments. Whether the two sets of results are correlated is currently under investigation. As the outgrowth of efforts to see if energization of kaolin could be achieved by mechanical stress also, Noam Lahav and I discovered a novel luminescent phenomenon in kaolin. Blue to near u.v. light is released by drying a water-wet paste of kaolin. The efficiency of this luminescent process, like TL and glycine oligomerization, is affected by thermal and radiative treatment of the kaolin. More recent studies have indicated that light is induced also when organic amines are added to, or removed from the kaolin surface. These luminescent properties also are influenced by thermal and gamma-irradiative treatments. Presently research efforts are being directed towards understanding the origins of desolvation-induced luminescence, both in terms of its molecular center and its modes of excitation. The role of the surface attraction of clay to water is being investigated using halloysites. The reactivity of the clay surface to glycine oligomerization is being explored in relationship to the electronic structure and excitation of kaolin. Correlations are being made between glycine oligomerization, electron-spin-resonance, thermoluminescence, solvation/desolvation-induced luminescences and kaolin absorption spectra as a function of heat and gamma-irradative treatments.

Prebiotic Formation of Phosphoanhydrides, like ATP, by Chemical Pathways that Resemble Fermentation (Glycolysis)

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All organisms require energy in a chemical form for maintenance and growth. Contemporary life obtains this chemical energy by the synthesis of the phosphoanhydride bond, such as that in ATP (adenosine-5'-triphosphate). Fermentation appears to be the simplest and probably most primitive method that organisms use to synthesize the "energy-rich" phosphoanhydride bonds of ATP. Fermentation is considered primitive because it does not require oxygen or light, and operates in solution without a need for organized compartmentation. The mechanism of formation of phosphoanhydride bonds in fermentation is called "substrate-level phosphorylation". Under anaerobic conditions substrate-level phosphorylations frequently occur by the oxidation of an aldehyde to give an "energy-rich" thioester, which is subsequently used to drive the formation of the phosphoanhydride bonds of ATP [aldehyde $\xrightarrow{\text{oxidation}}$ thioester $\longrightarrow$ phosphoanhydride bonds of ATP]. It is our contention that a related sequence of <u>non-enzymatic</u> chemical reactions provided the chemical energy needed for the origin of life on the primitive Earth.

The chemistry of this reaction pathway [aldehyde $\xrightarrow{\text{oxidation}}$ thioester $\longrightarrow$ phosphoanhydride bonds] is being studied in order to understand its role as a source of chemical energy for the origin of life. Thioesters have been formed in aqueous solution at neutral pH by (1) oxidation of acetaldehyde with a disulfide in the presence of ultraviolet light and (2) intramolecular oxidation-reduction of pyruvaldehyde catalyzed by a thiol. Thioester formation from glyceraldehyde is suggested by preliminary experiments that show thiol-dependent formation of lactic acid and glyceric acid from glyceraldehyde in solution at neutral pH. The significance of this reaction with glyceraldehyde is emphasized by the central energy-yielding role of glyceraldehyde-3-phosphate in the biochemical pathway of glycolysis. The formation of phosphoanhydride bonds with thioesters as the condensing agent has also been studied under prebiotic conditions. Acetyl thioester has been shown to drive the synthesis of the phosphoanhydride bonds of (1) pyrophosphate and tripolyphosphate under drying conditions, (2) phosphorylimidazole in aqueous solution and (3) pyrophosphate, tripolyphosphate and phosphorylimidazole in the presence of Ca^{+2} and water. "Energy-rich" thioesters have also been shown to bring about the synthesis of pyrophosphate on hydroxyapatite, a phosphate mineral. In these investigations products derived from radioactive substrates were separated by chromatography or electrophoresis and then measured with a radiochromatographic scanner.

EXPERIMENTS ON THE ORIGIN AND AMPLIFICATION OF MOLECULAR CHIRALITY

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The origin of optically active molecules in nature poses a question- intimately related to those of the origin of chiral biopolymers and of life itself- which has intrigued scientists since the time of Pasteur, but which still lacks definitive answers. During the intervening years a number of plausible physical mechanisms has been proposed for the abiotic genesis of chiral molecules, but experimental verifications of such mechanisms have been inconclusive or open to criticism. Because of the philosophical importance of the question, and since the validity of such mechanisms bears directly on the applicability of optical activity *per se* as a criterion for extraterrestrial or archaen life, we have reinvestigated a number of these mechanisms using modern experimental techniques. In general our approach has been to subject DL-amino acids (or derivatives), as prebiotically realistic substrates, to various chiral physical forces or environments, then to examine the recovered substrates for optical activity (i.e. an excess of one enantiomer, D ≠ L) using analytical gas chromatography, a technique superior for these purposes to conventional polarimetry. The several types of experiments which led unambiguously to the generation of optical activity were briefly the following: 1) DL-amino acids or certain derivatives proved subject to *ASYMMETRIC ADSORPTION* on the surfaces of finely powdered d- or l-quartz, with engendered enantiomeric excesses (e.e.'s) ranging from 1.5 - 12.5%; 2) DL-leucine underwent *ASYMMETRIC PHOTOLYSIS* with 212.8 nm right or left circulary polarized light, the e.e. reaching 2.5% after 75% photolysis; 3) in experiments designed to mimic natural β-decay electrons, the irradiation of DL-leucine with parallel ("right-handed") or anti-parallel ("left-handed") spin polarized 120 KeV electrons from a linear accelerator led to *ASYMMETRIC RADIOLYSIS*, with e.e.'s varying from 0.6 - 1.4%. These results were not subsequently duplicated using a different polarized electron source. β-Radiation and Bremsstrahlen from a number of natural β-emitting isotopes (^{90}Sr, ^{14}C, ^{32}P) led to no asymmetric radiolysis of DL-leucine, nor did irradiation with longitudinally polarized protons from a cyclotron. In these studies it was found that racemization of amino acids accompanied their exposure to ionizing radiation. Such *RADIORACEMIZATION* diminishes the efficacy of the above β-decay mechanism, and has been a separate subject in our more recent investigations.

The e.e.'s abiotically generated in the above experiments were typically only a few percent- smaller than might reasonably be thought adequate for the direct genesis of a primitive biosphere. Additional abiotic mechanisms for the subsequent chemical amplification of such small e.e.'s would clearly be stereochemically advantageous for a prebiotic molecular evolution toward the stereospecific biomolecular processes of the contemporary biosphere. More recent successful experiments, focused on potential mechanisms for the abiotic amplification of such small e.e.'s include the following: 1) D ≠ L Mixtures of leucine N-carboxy anhydride monomers having a known e.e. were subject to ca. 50% polymerization. The e.e.'s of the resulting polymers were examined (after hydrolysis), and found to be uniformly higher than the e.e.'s of the initial monomers, demonstrating that enantiomeric enrichment can occur during partial polymerization; 2) D ≠ L polyleucine oligomers of known e.e. were subjected to partial hydrolysis, and the e.e.'s of the recovered monomers and unhydrolyzed polymers were examined. The monomer hydrolysate leucines proved to have lower e.e.'s, and the unhydrolyzed polyleucine residual polymers to have higher e.e.'s than the original polyleucine oligomers, indicating that e.e. enhancement can occur in the polymer residue from the partial hydrolysis of an enantiomerically enriched polypeptide. On the basis of these sets of experiments a cyclic "polymerization-hydrolysis" mechanism has been proposed for the possible abiotic formation of enantiomerically homogeneous polypeptides on the primitive Earth.

Adsorption of Biomolecules (5'-Nucleoside Monophosphates and Amino Acids) Onto Homoionic Clay Surfaces

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Bernal in 1941 first suggested that clays may have played an important role in chemical evolution. The results of investigators since that time, and especially in the last 5 years, have lent proof to this hypothesis. More specifically, investigations have shown that selected metal ions substituted into the natural cation exchange sites on the surfaces of clays may have played a significant role in chemical evolution. Clay surfaces are of keen interest to prebiotic chemists and chemical evolutionists because they have recognized the possibility of specific adsorption and thus concentration of prebiotic monomers on these surfaces leading to condensation and production of bio-oligomers. The study of the interaction of significant biomolecules (e.g., 5'-nucleoside monophosphates and amino acids) with homoionic substituted clays should show whether these homoionic clay surfaces exhibit selectivity in interaction with these biomolecules. Such information is imperative to formulating intelligent conclusions concerning the likely role of homometallic clay surfaces in chemical evolution, especially as a template surface, and the relationship of the role of metal cations in the present day genetic apparatus.

The introduction of selected metal cations (Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Zn^{2+}) at the cation exchange sites in montmorillonite clay remarkably alters the binding behavior of biomolecules which normally do not bind readily onto the surface of naturally occurring montmorillonite clay in an aqueous environment. Using only aromatic biomolecules we have observed larger binding for 5'-AMP over 5'-CMP and Trp over Phe on homoionic clay surfaces. The order of binding selectivity of clays substituted with a metal cation for the different aromatic biomolecule ligands varied within the nucleotides and amino acids used. Adherence to the Irving-Williams metal-ligand binding series was not observed in all cases; selectivity in binding of a metal cation situated in a cation exchange site on a clay surface seems to be more complex than homogeneous, aqueous metal ligand binding. A series of nonaromatic amino acids (gly, ala, β-ala and sarcosine) are also being studied.

SESSION III

INFORMATION TRANSFER

NMR STUDIES OF INTERACTIONS BETWEEN NUCLEIC ACIDS AND PROTEINS

by

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The origin of life on earth is inextricably intertwined with the origins of the genetic code. Since the present-day biological processes include both replication and information transfer, the study of these phenomena may provide some clues to the emergence of life. As an approach to the problem, we have chosen to study the specific physical chemical interactions between constituents of nucleic acids and proteins.

Nuclear magnetic resonance spectroscopy can provide data on such relationships. The availability of sensitive NMR instrumentation and comprehensive computer facilities make it possible to investigate some of the basic questions with regard to the nature of interactions between, mono-, di-, tri-, and oligonucleotides and mono-, di-, tri-, and oligopeptides.

In our preliminary studies of AMP/l-Phe-OMe interaction, we have found that:

1. Mg^{2+} affects the protons of 5' AMP involved in the Phe interaction

2. the signals of the 5' AMP ring protons are shifted downfield by the presence of Mg^{2+}

3. L-Phe-OMe appears to bind to the 5' AMP (anti-codon monomer) more tightly than to the 5' UMP (codon monomer)

4. interactions between 5' AMP and various dipeptides (gly-tyr, gly-phe) results in downward shifts of ring proton signals.

These results may contribute to our understanding of the nature of the relationship between nucleic acids and proteins.

CYANAMIDE MEDIATED PREBIOLOGICAL SYNTHESIS OF PHOSPHOLIPIDS, OLIGOPEPTIDES AND OLIGONUCLEOTIDES

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In the study of chemical evolution one of the most important reactions is the condensation of monomers into biochemical compounds which are essential for life processes. These include phospholipids, oligopeptides and oligonucleotides. Phospholipids are presumed to be necessary for the formation of bilayered membranes, oligopeptides for catalysis, and oligonucleotides for replication. This step in chemical evolution is crucial not only because of the relevance to life of the synthesized compounds, but also because it has to be carried out under geologically plausible conditions compatible with the emergence of life. Work carried out in our laboratory during the past years has shown that these three types of compounds can be synthesized in aqueous systems by means of cyanamide.

Using a primitive Earth evaporating pond model the prebiotic synthesis of phosphatidylcholine was accomplished for the first time when a reaction mixture of choline chloride and di-sodium phosphatidate, in the presence of cyanamide was evaporated for a few hours. Optimum yields of about 15% were obtained at 80°C. The synthesis was also observed at lower temperatures. Similar conditions led to the synthesis of another vital phospholipid, phosphatidylethanolamine. Membranous structures in the form of oligolamellar and multilamellar liposomes were readily obtained from these prebiotically synthesized phospholipids. The synthesis of three histidyl peptides in yields of up to 11% was demonstrated when aqueous solutions of histidine, leucine, cyanamide, and $MgCl_2$ were evaporated and heated for 24 hrs at 80°C. Although the above syntheses occur better at a slightly acidic pH the formation of these compounds was also demonstrated for systems adjusted to pH 7 with NH_4OH. For the synthesis of oligonucleotides the evaporation pond model can be modified and made more effective. Thus a reaction system incorporating several consecutive cycles of evaporation leads to the rapid synthesis of oligonucleotides up to at least the tetranucleotide in yields of more than 20%. This system has a high degree of prebiotic plausibility in that the reaction proceeds well at 37° and 60°, it uses the unactivated nucleoside monophosphate, it occurs at neutral pH in the presence of ammonium chloride, and the prebiological agent cyanamide is more efficient at producing oligomers longer than the trimer than is a chemical condensing agent in the carbodiimide family. Of a number of condensing agents tested, cyanamide is the most active under the simulated prebiological conditions mainly due to stereochemical effects. Several poly amino acids (poly His, poly Arg) increase the yield of condensed product in the presence of cyanamide which, in line with our earlier observations show that imidazole also increases the yield. A discussion of the role of cyanamide, imidazole and arginine derivatives leads to the conclusion that a proton relay mechanism between the (N=C-N)-group common to the above three compounds may be operating in the prebiotic synthesis of the phospholipids, oligopeptides and oligonucleotides. Also a similar mechanism may be responsible for similar syntheses in living systems catalyzed by the imidazole and arginino groups of the corresponding enzyme active centers. Prebiotic cyclic processes imposed by external factors is a way to reconcile the nearly opposite conditions required for oligomerization and replication. An obvious next step is to attempt a prebiotic template directed oligomerization using simple or unactivated nucleoside monophosphates in such a system. This work was done with the collaboration of J. Eichberg, M. Rao, D. Odom, J. Hawker and T. Yamrom.

AN RNA POLYMERASE MODEL

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We have developed an RNA polymerase model in which a poly(C) template directs an efficient synthesis of oligo(G)'s up to at least the 40-mer. The reaction proceeds in a Watson-Crick double helix and has high regiospecificity and fidelity.

Mixed templates containing an excess of C direct an efficient synthesis of mixed oligomers containing an excess of G and smaller amounts of the bases complementary to the minor constituents of the template. Bases whose complements are absent from the template are not incorporated into product.

Self-Ordering → Reverse Translation?

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The track of molecular evolution has been followed from non-random polymerization of sets of amino acids through early informational cells into the beginnings of cellular metabolism. The polyamino acids characterized as precursors of living cells reveal order of a kind that is consistent with a context of recent inferences by astrophysicists of a Universe that was ordered from the beginning, at another level. The extensively verified fact of self-sequencing of amino acids makes a consistent overview out of the interpretation that thermal proteins (proteinoids) could have served as the first bioinformational molecules and the first specific metabolic catalysts. The microspherical aggregation products of the proteinoids (microspheres) have been found to be either less heterogeneous in size or more heterogeneous in size than microfossils or modern algae. Some artificially fossilized microspheres are indistinguishable from algae artificially fossilized by micropaleontologists.

The most recent research has shown that thermal proteins containing sufficient basic amino acid catalyze the synthesis of peptide bonds between all types of amino acid. Such polymers function as catalysts in solution, in proteinoid microspheres composed of both acidic and basic proteinoids, and in complexes of basic proteinoids and polynucleotides. The energy-providing agent can be either pyrophosphate or ATP; both high-energy phosphate and catalytically active lysine-rich proteinoid are, however, needed. Repeated infusion of ATP results in higher yields of peptide than does a single batchwise inclusion of the same total amount of ATP. The identity of the polynucleotide in polynucleotide-proteinoid complexes influences the proportion of gly-phe and phe-gly synthesized from gly and phe. Extension of the phenomena observed, plus an earlier demonstration that basic proteinoids catalyze the formation of internucleotide bonds, are allowing an experimental modelling of the recently revived concept of reverse translation.

Possible Pathways Towards the Evolution of the Genetic Code

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The study of chemical evolution was so far able to uncover possible pathways for the prebiotic synthesis of practical all small building blocks of the biochemicals of living systems. It has further thrown considerable light on the several ways of spontaneous synthesis of oligomeric peptides and RNA-type nucleotides. However, because of systematic and synthetic difficulties, bio-oligomer-studies were carried out on systems of only one kind, e.g. protenoids, sugars, nucleotides. We know next to nothing about possible effects of the developments of one type of potential bio-molecules on another, let alone about any evolutionary interaction that might have formed the basis for the occurrence of amino-acid sequences, base pair coding, or reaction aiding stereochemical configurations as precursors of enzymatic sites.

Studying the polycondensation of adsorbed activated amino acids (AA) we established the adsorption isotherms of AA's and nucleotides, the existence of specific molecular weights related to the type of adsorption, and we observed also peculiar ways, by which preadsorbed peptides affect MW of the next generation.

We are working now on adsorption isotherms of the principal participating nucleic acid components and also on the co-adsorption of AA's and peptides with purine-pyrimidine bases and their nucleotides. As a result we expect to assist the adsorption of AA's by adsorbed nucleotides, also to help the adsorption of the latter by preadsorbed bases, and we are looking into the possibility that the interaction of growing nucleotides and AA's might lead to a development of primitive complexes.

Whatever the results, they should cast some light on a possible regular co-evolution of these primitive building blocks for emerging life, on potential interactions that led to the evolution of the genetic code and to the emergence of some protenoids with enzymatic capabilities.

THE CHEMICAL BASIS FOR THE ORIGIN OF THE GENETIC CODE AND THE PROCESS OF PROTEIN SYNTHESIS

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Certainly it is one of the defined characteristics of contemporary living things that they respond to environmental changes (stimuli), not only by simple, direct, and predictable chemical reactions, but also by indirect, complex, nucleic acid mediated responses requiring the synthesis of mRNA and then active principles, protein. One of NASA's goals is to understand how life originated, and our efforts to understand how the process of protein synthesis and the genetic code came to be are an essential part of that understanding.

Conceptually, the problem has two parts: (1) the chemical reactions involved in the process of protein synthesis, and (2) the consistent relationship between sequences of nucleotides in nucleic acids and amino acids in proteins. As a result of this conceptual composition of the subject, our effort has had two components: (1) a study of the chemistry of activated aminoacyl species, and (2) an attempt to deduce correlations of properties and selective affinities between amino acids and nucleotides. The chemical studies have shown that all of the reactions, from initial activation by ATP to peptide bond formation, are spontaneous. These studies have included activation of amino acids by ATP, transfer of amino acids from nucleotide anhydride to ester mediated by imidazole, and hydrolysis and attack by nucleophiles, including peptide formation. Data from our laboratory and others have shown that the genetic code is far from random, and reveal direct correlations of a number of properties between amino acids and their anticodonic nucleotides. Furthermore, by a variety of techniques, principally NMR, we have now begun a collection of binding constants between amino acids and nucleotides. These binding constants, though low (i.e. $< 10\ M^{-1}$), consistently show selective affinities between amino acids and their anticodonic nucleotides. For example, binding constants of the amino acid, phe, for the four common nucleotides are $6.6\ M^{-1}$ (AMP) $> 3.5\ M^{-1}$ (GMP) $> 2.1\ M^{-1}$ (CMP) $> 1.1\ M^{-1}$ (UMP). These data probably explain why the only anticodons of phe contain AAPu (3' → 5'). In addition, a number of studies have shown that, of the hydrophobic amino acids (phe, leu, ile, val, met) having "A" as the middle, most important anticodonic letter, phe has the greatest affinity for adenine derivatives. Studies of the reaction of this same set of amino acids with ATP have shown that the rates of reaction are correlated with the affinity of the various amino acids for adenine derivatives.

From these kinds of data, a general principle has emerged - namely, that the rates of various chemical reactions between amino acids and nucleotides are a function of the degree of affinity between the reacting species. Consequently, our present working hypothesis is that the genetic code and its attendant process of protein synthesis arose as a consequence of selective affinities between amino acids and their anticodonic nucleotides.

NUCLEIC ACID TEMPLATE PROPERTIES

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During the past few years progress has been made in the area of non-enzymatic synthesis of oligonucleotides in the presence of polynucleotide templates (Orgel and coworkers). Prominent among the factors influencing the effectiveness of these reactions are template composition, specificity of ions and the nature of activating groups.

One of our aims is to explain in molecular terms why are polypyrimidines effective templates and polypurines not. Calculations of helical structure preferences depending on sequence will be presented. Since the prerequisite of template facilitated condensation is the formation of Watson-Crick, type helicies, the conformational preferences and stabilities of both the template and the single base stacks are paramount for the outcome of the reaction. Stabilization by specific ionic bridges may further influence the conformational choices. The presented data will illustrate the effect of these factors and show that template efficiency is a result of a subtle interplay between sequence dependent conformational stabilities and helix compatabilities (2'-5' or 3'-5' linked nucleotides).

Another interesting aspect of these reactions is the sequence length distributions of the formed oligonucleotides. A stochastic model will be outlined for simulating the kinetic and chain length distribution of a synthesizing oligonucleotide. The first step of the program constructs binding isotherms for a mixed population of single and oligonucleotides. The reaction probabilities for elongation of different species at each time interval are decided according to the state of the binding isotherms.

In addition, energetics's of various base mispairs will be presented together with calculated mutation probabilities. The aim of this study is to estimate the frequency and type of mutations which could have occurred during the replication of prebiotic double helical oligonucleotides and polynucleotides.

Finally, models of nucleotide-peptide complexes constructed from studies of present day protein-nucleic acid complexes will be presented and discussed. The emphasis will be on the examination of these complexes as possible structures involved in the origin of the coupling between the two informational macromolecules as well as the start of gene regulation.

The significance of these studies should be in the potential usefulness for designing effective heteronucleotide templates in further prebiotic synthetic experiments.

The Influence of Water on the Stability of DNA Base Pairs

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One of the fundamental problems associated with the study of the origin of life is that of information storage and transfer. Those factors that affected the stability and polymerization of polynucleotides in pre- and proto-biotic environments would have dictated the kind of process that would emerge as functional in living organisms. Single stranded structures would not be as good as double stranded as candidates for primary information storage molecules because exposure of the nucleic acid bases to the solvent would increase susceptibility to chemical modification and mutation. Thus, in pre- and protobiotic systems, the double stranded structures that would be formed during replication would impart considerable stability to stored genetic information. While double stranded nucleic acids are thermodynamically stable in an aqueous environment and do not dissociate readily into separate strands, they could not be so stable as to be unseparable at the time of replication in prebiotic systems that lacked the specialized enzymes of extant replication. This essential balance between stability and separability, is brought about by a delicate interplay between hydrophilic and hydrophobic effects, and is an important factor in the stability of the DNA helix in living systems today.

It was assumed for some time that the stability of nucleic acid resulted exclusively from hydrogen bonding. Experimental data on isolated base pairs has cast doubt on this assumption. It has been established that in water, isolated nucleic acid bases associate by stacking interactions. In nonpolar solvents, however, base pairs do associate by hydrogen bonding. To investigate the basis of the stability of the DNA helix in aqueous solution we have performed Monte Carlo simulations of stacked and planar associations of the nucleic acid bases adenine and uracil in both polar (water) and nonpolar solvents (e.g. CCl_4). These simulations use mathematical models of molecular structures, various model representations of the forces that attract and repel the atoms of the molecules, and permit the exploration of the behavior of base or solvent molecules in realistic volumes, and at selected temperatures and pressures. Our results show that in a nonpolar environment planar association of A-U is favored bu 8 kcal/mole over stacked self-associations, while in aqueous solution the opposite is true. These results can be interpreted in terms of a balance between solute-solvent and solvent-solvent interactions and give us a unique insight into the role that electrostatic and dispersion forces play in polar and nonpolar solutions.

SESSION IV

SOLAR SYSTEM EXPLORATION

NEW GC COLUMNS FOR INVESTIGATION OF THE ATMOSPHERES OF TITAN AND THE OUTER PLANETS

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The accurate measurement of atmospheric constituents of extraterrestrial bodies, planets, moons or comets, may provide more concrete information on which to base hypotheses about the origin and evolution of the solar system, chemical evolution and life. Previous missions to Mars and Venus measured atmospheric constituents by gas chromatography using state of the art technology. However, missions to bodies much more distant require that the instrumentation used on those flights be significantly reduced in power, weight and volume requirements and that sensitivity be increased. These factors have necessitated the miniaturization of many of the component parts of a gas chromatograph and that includes the development of new column technology to be compatible with the more sensitive detector system.

Measurement of hydrocarbons in the atmospheres of target bodies is one major objective and since the conventional liquid hydrocarbon phases were unusable because of bleed, it was necessary to investigate chemically bonded materials using porous silica as a base. Various syntheses were carried out, taking advantage of the silanol groups available for derivatization. Amino silica was made and modified with other compounds in such a way that aromatic amides, urea, and Schiff base surfaces were made as well as directly derivatized silica which produces urethane surfaces. Columns which will separate the reported hydrocarbons on Titan have been made and are reasonably short (75 cm x 1 mm), light, and analysis time is fast and, using the metastable ionization detector, sensitivity is at the ppb to sub ppb level. Further column development is continuing to develop and reduce in size, weight and volume, columns which will separate the permanent gases and more polar organics and water.

LIMITS OF IN SITU DETECTION OF VOLATILES IN SOLAR SYSTEM EXPLORATION

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Measurements of volatiles associated with extraterrestrial bodies are an integral part of studies pertaining to biological compatibility, ecology, the chemical history of the solar system, and the origin and evolution of life. The confirmation and refinement of remote-sensing data on chemical composition through in situ analysis has become a reality with the successful Viking and Pioneer-Venus missions. The early designs of analyzers for volatile, or volatilizable, chemical species have been improved with the goal of reducing weight and power requirements, and increasing the sensitivity and resolution of the instruments.

The sensitivity of gas chromatographs and parallel mass spectrometers used as flight instruments has reached comparable magnitude. The GC thermistor detectors deployed with the Viking and Pioneer-Venus missions are being replaced by ionization devices that are sensitive in actual situations to the parts-per-billion level and can be adjusted to register concentrations from that level upward over a large dynamic range. The new devices are of miniature dimensions, shock-resistant, reliable, and thermally and pneumatically stable. Specific response to all molecular species is non-selective and does not depend on chemical complexity.

ANALYSIS OF COMETARY DUST BY GAS CHROMATOGRAPHY

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Comets are primitive solar system bodies which release large quantities of gas and dust during their transit of the sun. Being very primitive, they contain information about the early history of the biogenic elements that may not be found anywhere else in the solar system. Specifically, information about the biogenic elements may be found in the volatile and nonvolatile molecules associated with the released comet dust. These molecules, many of which may be comprised of the biogenic elements, include surface absorbed, chemically bound and those internal to the stable host. Collecting comet dust and subsequently measuring the associated volatiles will therefore provide an understanding of the early history of the biogenic elements as related to chemical evolution. In future efforts to study these particles, both remotely and with a returned sample, only very small samples will be available. Therefore, a highly sensitive analytical instrument is needed to analyze the small quantities of volatiles released from the available cometary dust. The gas chromatograph is such an instrument.

A laboratory prototype of a flight gas chromatographic system based on recent advances in the state-of-the-art has been assembled specifically to analyze volatiles associated with cometary dust. The dust samples are heated stepwise to pyrolysis temperatures and the released volatiles are then separated on a highly efficient gas chromatographic column and measured with a very sensitive detector. Model comet dust, such as carbonaceous chondrites, have been incrementally heated and the released volatiles measured. For example, from a Murray meteorite sample heated to 750°C, H_2, N_2, CO, NO, CH_4 and CO_2 were evolved which were readily detected and measured. It is estimated that sub-microgram samples would allow measurement of volatiles in the ppm range if the particles resemble CM carbonaceous meteorites.

MULTIPLEX CHROMATOGRAPHY FOR SOLAR SYSTEM EXPLORATION

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Determination of molecular species comprised of the biogenic elements in the atmospheres of planets and moons of the solar system is one of the foremost requirements of the exobiologist studying chemical evolution and the origin of life. Flight experiments have been conducted on both Mars and Venus in the past and a wealth of data has been acquired by the gas chromatograph, mass spectrometer and gas chromatograph/mass spectrometer. Future missions to explore Saturn, Titan, Mars and Venus will require advanced instrumentation concepts which are highly sensitive, efficient, physically small and capable of analyzing complex mixtures. Recent advances in gas chromatography suggest that conventional gas chromatography is still one of the most practical methods available to conduct the desired analyses in future constrained missions, but limitations in the technique still exist which can be alleviated with multiplex chromatography.

Multiplex chromatography is a technique where many samples are psuedo-randomly introduced to the chromatograph without regard to elution of preceding components. The resulting data is then reduced using mathematical techniques such as cross-correlation or Fourier Transforms. Several advantages are derived from this technique. A signal to noise ratio increase of several orders of magnitude may be realized since all random noise may be effectively discarded. Further, because there is no need to wait for the last component of a analysis to elute before starting the subsequent analysis, many more analyses can be conducted in a given length of time. This would be particularly useful in an atmospheric probe mission where there is a discrete amount of time available for the mission. To demonstrate the capabilities of multiplex chromatography for future solar system exploration, a sampling system or chemical modulator has been developed which offers many advantages over previously reported mechanical samples or modulators. Samples under analysis are merely absorbed and desorbed from a small bed of selectively sorptive material thus eliminating all mechanical devices from the chromatograph.

SESSION V

PLANETARY PROTECTION

PROPOSED NEW POLICY FOR PLANETARY PROTECTION

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In order to control contamination of planets by terrestrial microorganisms and organic constituents, U.S. planetary missions have been governed by a planetary protection (or planetary quarantine) policy which has changed little since 1972. This policy has recently been reviewed in light of new information obtained by planetary exploration during the past decade and because of changes to, or uncertainties in, some parameters used in the existing quantitative approach. On the basis of this analysis, a new planetary protection policy, with the following key features, is proposed: deemphasizing the use of mathematical models and quantitative analyses; establishing requirements for target planet/mission type (i.e., orbiter, lander, etc.) combinations; considering sample return missions a separate category; simplifying documentation; and imposing implementing procedures (i.e., trajectory biasing, cleanroom assembly, spacecraft sterilization, etc.) by exception if the planet/mission combination warrants such controls. Interpretation of the new policy for missions like Galileo, Mars Surface Sample Return, Saturn Orbiter with Twin Probes, and missions to comets are considered. In general, the new policy proposes elimination of all but documentation requirements for most planetary missions and simplification of the remaining compliance procedures.

SESSION VI

FUTURE DIRECTIONS

The Biogenic Elements and their Compounds: The Astrophysical Context

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Abstract

The chemical elements that served as raw materials for life-forming processes had a long and complex history prior to their presence in the terrestrial atmosphere. A NASA Study Group on the Cosmic History of the Biogenic Elements and Molecules has recently reviewed our current understanding of the pre-planetary evolution of these materials.

The biogenic elements (principally C,N,O,H) were formed by thermonuclear processes in the interiors of previous generations of stars, and expelled to the interstellar medium by stellar winds and supernova explosions as atoms, molecules, and condensed dust particles. This inventory of materials was changed in the interstellar medium by photochemical and other types of reactions, producing (among other things) the array of organic molecules detected in space by radio and IR spectroscopy, and also possibly complex refractory polymers on grain surfaces. The system was further modified chemically during self-gravitative collapse of a volume of the interstellar medium to become the protosun and solar nebula, and in the nebula as it evolved. Organic materials from the nebula were trapped in the planetesimals as they aggregated, and to varying degrees altered in them by thermal and hydrothermal metamorphism. Samples of primitive solar system organics at this stage of their evolution are preserved for our study in meteorites.

THE GALAPAGOS HYDROTHERMAL VENT ECOLOGIES: POSSIBILITIES FOR NEOABIOGENESIS?

by

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Recent discoveries of complex ecologies at hydrothermal vents on the ocean floor have opened up new areas for research into the origins of life on Earth and the evolution of communities of micro-organisms under extreme environmental conditions. Under such conditions, the question of neoabiogenesis appears to be a tantalizing possibility.

In order to explore these opportunities, the Laboratory of Chemical Evolution of the University of Maryland organized a workshop at the Belmont Conference Center, Elkridge, Maryland on April 22-24, 1982. A group of scientists familiar with the phenomena of the vents, and selected from the fields of biology, chemistry, and geology, presented the data available on the characteristics of this unusual environment.

Enormous fluxes of solvent and solute result in the formation of gradients of pH, temperature, and concentration of chemical species. The vents are capable of sustaining populations of micro-organisms of thermophiles, mesophiles, anaerobes, chemoautotrophs, etc. The rich "organic broth" seems to serve as an excellent source of food for the megafauna. It is generally believed that all the conditions suitable for the origin of life have disappeared from the earth. Perhaps such conditions are found today providing the opportunity for investigating the concept of neoabiogenesis.

THE EVOLUTION OF COMPLEX AND HIGHER ORGANISMS

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The existing NASA Planetary Biology Program has dealt with chemical evolution and the origin and early evolution of life, but has not examined events after the late Precambrian. To explore the possibility of filling out the program to cover the Phanerozoic, a group of scientists met in a series of science workshops over the past year to examine the major questions involved.

We made the following assumptions: (1) The starting point, in the evolutionary sequence, would be the appearance of multicellular organisms, some one billion years ago; (2) All phases of the evolution of complex life would be addressed, up to and including primates; (3) Special attention would be given to the interaction between the evolving biota and the physical and chemical characteristics of the environment; (4) Special emphasis would be placed on evolutionary changes which might be related to events in space, namely astrophysical phenomena, solar disturbances, earth moon interactions, solar system dynamics and asteroid and cometary impacts; (5) Attention would also be given to the study of the possibilities for the existence of complex life elsewhere in space.

The draft of our report is now in preparation. Each chapter deals with current views and gives recommendations for research areas of importance. The chapters deal with the following topics: (1) The geologic history of complex organisms; (2) Physico-chemical environments; (3) The evolutionary process; (4) The effects of extraterrestrial phenomena; (5) The potential for complex life elsewhere in space.

The report will go to press in November 1982, and should be published in May 1983.

ROLE OF EXOBIOLOGICAL SCIENCE IN THE FUTURE OF SOLAR SYSTEM EXPLORATION

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A rational approach to the space exploration of the solar system has to include all the aspects of physical, chemical and biological science which are relevant to such an exploration. We need to know not only the compositional, structural, and dynamical aspects of the present solar system, but also how it was formed from interstellar matter and how did life originate in our planetary system. Two fundamental principles which have emerged as the result of exobiological research performed during the past two decades are the following: A. The origin and evolution of life where it occurs, is probably an integral part of the physical and chemical processes that go into the formation and evolution of the planets. B. Once life has originated on a planet (Earth) its presence causes major changes in the parts of the planet which interact with the biosphere. From then on the physical evolution of the surface, hydrosphere, and atmosphere of the planet is significantly influenced by life. Therefore, we need a comprehensive understanding of the general process of planetary evolution which has culminated in the emergence of life in at least one case, and the impact of this life in the future evolution of the planet. More specifically, the three major questions that have to be answered to provide this understanding are: 1. What can the study of extraterrestrial organic chemistry tell us about the prebiological chemical era on Earth and elsewhere? 2. How did the formation and earliest history of the Earth set the stage for chemical and early biological evolution?, and 3. Once life has emerged, what is the impact of the evolution of life on the Earth's planetary evolution?

Both terrestrial and extraterrestrial investigations are required to answer these questions. In approximate order of priority the primary targets for solar system exploration of interest to exobiological science can be divided into three major groups: (a) Small primitive bodies, namely comets, asteroids, meteorites, and interplanetary dust. (b) Giant planets and their satellites, with special emphasis on Titan and Europa. (c) Terrestrial planets and their satellites, essentially Mars, Phobos, Deimos, Venus and the Moon. Beyond the solar system some of the comparable primary targets are: (d) Circumstellar and interstellar clouds, (e) Dense and gravitationally contracting nebulae, as analogs of our primeval solar nebula, and (f) Non-luminous bodies orbiting other solar-like stars, as analogs of planets in our solar system. In this case both ground-based and orbital telescopes can be used to make measurements of exobiological relevance by means of visible, IR., or microwave spectroscopy. With the information obtained from the above targets we may be able to answer the first question (1 above). To provide answers for the second and third question (2 and 3 above) will require an in depth study of the Earth by comparative planetology and by direct observation, in situ, or from orbital spacecraft. It is well understood that a complete understanding of the origin and evolution of life on the Earth will not be possible without parallel studies in terrestrial laboratories providing the necessary experimental support to the above exobiological exploration of the solar system and beyond. There appears to be a general consensus on this approach among the scientific community as indicated by the recent report "Extraterrestrial Exploration and the Origin of Life", edited by R. S. Young. A more detailed discussion of the priority targets of interest to exobiological science will be presented.

The Status of SETI Research

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Detailed studies of the SETI problem have been made over the last few years by the ad hoc "SETI Science Working Group" (SWG) established with NASA sponsorship. These studies have reconfirmed the idea that the most promising approach to the detection of other civilizations or, indeed, perhaps extraterrestrial life, is through a search for microwave radio transmissions. The most important need is the ability to search large portions of the radio spectrum with good radio frequency resolution. New low-cost integrated circuit chips have solved this problem, and a design and appropriate prototypes exist for the construction of a multi-channel spectrum analyzer (MCSA) of reasonable cost. It would provide coverage of over 8 million channels simultaneously, and would be utilized with dedicated computers and appropriate software to conduct an automatic, generalized search of the energy collected by a radio telescope for evidence of signals of intelligent origin. As planned by the SWG, the MCSA would be used with existing large radio telescopes to search the entire visible sky over a wide range of frequencies for strong signals, and a large number of directions of special interest, such as the direction to near-by sun-like stars with greater sensitivity. This program would increase the parameter space searched for signals by a factor of roughly a million over the space searched in all previous attempts.

In the meantime, a much smaller version of the MCSA, funded privately, has been used in a search which tests many of the concepts in the NASA plan. In the USSR a number of large SETI programs are underway. One program involves the construction of some one hundred small antennas specifically to give good sky coverage for SETI, and another is associated with a new high precision 70-meter telescope now under construction near Samarkand.

SESSION VII

GEOLOGICAL RECORD

ASPECTS OF EVOLUTION AND DIVERSITY OF PRECAMBRIAN LIFE: ARCHEAN AND PROTEROZOIC

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It is perhaps fair to say that the study of the origin and evolution of Precambrian life is parodoxically both frustrating and highly rewarding. It is frustrating in that much of this immense period of earth history provides only a fragmented though highly significant record of ancient life. The sedimentary-metamorphic history of the solid earth has recently been extended back to ca. 3.8 b.y. in the Isua supracrustals of Greenland; the credible morphological record of life extends back to ca. 3.4-3.5 in the Swaziland Sequence of South Africa and possibly in sediments of the Pilbara Block of Western Australia. The study of Precambrian paleobiology is rewarding in that the known tangible record conforms to a logical theoretical model of evolution from isolated single-celled organisms through stages of colonial to multicellular organisms to the evolution of distinct microbial ecosystems by late Precambrian time.

If we eliminate the alleged "fossils" from the Isua metasediments as of abiotic and indeed purely mineralogical origin, the earliest discrete entities which may be considered truly biological are the carbonaceous microspheres from the early Precambrian upper Onverwacht sediments of South Africa. The evidence is based on both morphology, their presence in aggregates of organic clasts, and in their size-frequency distribution patterns of which closely resemble those of steady-state populations of extant algal unicells. Also, certain of the microstructures have been preserved in the configuration of binary cell division. The ratios of the stable isotopes of carbon ^{13}C and ^{12}C ($\delta\ ^{13}C$) of their organic matter and its matrix are also consistent with their biogenic origin ($\delta\ ^{13}C$ = -25 to -30).

A major "benchmark" of the level of early Precambrian microbial evolution is abundantly represented in the ca. 2 b.y. old Gunflint iron formation, Lake Superior region. At least 16 taxa of microfossils, some of questionable affinity with any known extant organisms, can be recognized. These represent a wide range of morphological diversity within the realm of prokaryotic life. None of them can be regarded as of unquestionable eukaryotic origin, on the basis of either size or histology. The more significant elements of the Gunflint microbiota will be discussed. Significant microbiotas of essentially Gunflint age recently have been described from the Belcher Islands, Hudson Bay, Canada, and the Duck Creek basin of Western Australia. The wide geographic spread of now known microfossil assemblage of about 2. b.y. age are putative evidence of a world-wide thriving biosphere by mid-Precambrian time.

As we proceed upward in Proterozoic sequences in various geographic areas of the earth the number of microbial occurrences on the existing continents increases. Among the richest and most diverse of these are the Bitter Springs Formation of central Australia (ca. 800 - 900 m.y.), and a recently discovered and yet unpublished biota from the Narssaessuk Formation of northwest Greenland. These show increasingly more complex morphology. Of the late Precambrian assemblages, one, though not taxonomically rich possesses members of the biota such as acritarchs and large unicells of such size (>80. -100μ) that they provide evidence of eukaryotic affinity. Crucial evidence for the time of emergence of unquestionable eukaryotic life would be the discovery of reproductive organs or sexual reproductive stages, a circumstance well within the realm of possibility in view of the remarkable preservation now known in Precambrian sediments.

ARCHAEAN STROMATOLITES FROM ZIMBABWE: EVIDENCE FOR ENVIRONMENTAL CONDITIONS

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The only direct evidence we have for life in the Archaean is the occurrence of algal stromatolites. To the extent that they can give us clues as to their growth environment, we gain knowledge of the general environmental conditions of the Archaean. Unfortunately, most stromatolites of that age have been subjected to some degree of alteration, which clouds the picture. Some of the best preserved stromatolites of Archaean age are to be found in Zimbabwe, in the Cheshire, Manjeri and Mushandike formations. Cores from these algal limestones have been examined in some detail using a variety of analyses, including stable isotope ratios of carbon and oxygen, various inorganic elemental analyses, and the petrology by thin sections.

Thirty cores were obtained from the three formations during the summer of 1981. The various domains of carbonate were examined for $\delta^{18}O$, $\delta^{13}C$ and Fe, Mg, Mn, Sr and Rb. The Cheshire and Manjeri formations (age 2.7 b.y.) show $\delta^{18}O$ values of -8 to -13‰ (PDB) and $\delta^{13}C$ values for kerogen of -26 to -35‰ (PDB). The magnesium content is low, seldom exceeding 2%, even in the most dolomitized areas. Rubidium concentrations run about 50 ppm, while strontium is quite variable. Rubidium-strontium isochrons are being attempted. There is a substantial quantity of mineral-bound water in these algal limestones, and D/H ratios in the fraction of water released at about 550° is being examined.

In thin section, textural preservation is often excellent, although some early recrystallization is commonly seen. The best preserved Cheshire samples show a wide variety of primary structures, and there is no evidence for the pervasive passage of post-lithification fluids through the rocks. Some preserved algal structures seem to be present.

It has been a disappointment that the cyclical nature of the Cheshire formation (22 cycles in the 50 meters of thickness) does not show up in any significant variations in oxygen isotope content. Minor changes are clearly evident in the elemental analyses, however.

The evidence from the thin sections for a closed system, and the negative values of the oxygen isotope ratios argue for an ocean temperature near 50°C, but further work is necessary before this can be defended with any certainty.

GEOCHEMISTRY OF CARBON IN THE LOWER CRUST AND THE HISTORY OF THE CARBON CYCLE ON EARTH

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Studies of ancient life are severely constrained by our limited knowledge of the earliest terrestrial environment. This environment was influenced, perhaps profoundly, by volatiles emanating from the earth's interior. This presentation discusses the nature of carbon in present-day emanations and attempts to interpret its significance for studies of ancient life.

Today, most "juvenile", deep crustal carbon emanates from the vast mid-oceanic ridge system. The present rate of carbon emanation would require more than three times the age of the earth to accumulate the present inventory of sedimentary carbon. Within the uncertainty of the measurements, the average carbon isotopic composition of the total sedimentary reservoir is identical to that of the juvenile carbon, which occurs both in midoceanic basalts and in the hydrothermal fluid. This similarity indicates that the average carbon isotopic composition of the earth's sedimentary reservoir has been remarkably constant over geologic time.

Concerning the chemical state of juvenile carbon, several measurements of carbon dioxide and hydrocarbons have been made in geothermal localities. Molecular carbon isotopic data indicate that most, if not all, of the hydrocarbons contributed by continental geothermal systems derive from thermal decomposition of organic matter in sedimentary rocks or groundwater. The origin of the methane which emanates from marine hydrothermal systems is still uncertain.

THE OXYGEN ISOTOPIC RECORD IN PRECAMBRIAN KEROGENS

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Research in our laboratories comes under the heading of "isotopic biogeochemistry." Specific investigations range from studies of the enzymatic control of the distribution of carbon-13 within biosynthetic products [Monson and Hayes, JBC 255, 11435 (1980); GCA 46, 139 (1982); JBC 257, 5568 (1982)] to isotopic studies of Precambrian kerogens [Hayes, et al., in press]. All of these studies are aimed at reconstructing the record of biochemical evolution. On the one hand, the study of isotopic fractionations characteristic of modern systems provides baseline information about the isotopic signatures of specific environments and biological processes. Further, study of the Phanerozoic geochemical record allows recognition of post-depositional alteration processes that can affect isotopic signals initially carried by the biological input. On the other hand, isotopic studies of ancient kerogens, when combined with this baseline information, can help to define the timing of major events in biochemical evolution. For example, the record of carbon-13 abundances in Precambrian kerogens has been interpreted in terms of the origin of autotrophic carbon fixation prior to 3.5 Ga ago; the origins of methanogenesis, oxygenic photosynthesis, and methylotrophy prior to 2.7 Ga ago; and the gradual rise of multicellular organisms in the interval between 2.0 and 0.8 Ga ago.

The record of oxygen isotopic abundances in sedimentary organic matter is completely unexplored, primarily because of analytical difficulties (methods for the quantitative conversion of organic oxygen to CO_2 have been lacking until very recently). Now, however, we have adapted the methods developed by others [Thompson and Gray (1977), Brenninkmeijer and Mook (1980)] for the analysis of pure cellulose to the analysis of oxygen-18 both in pure compounds and in the more complex organic materials found in geological specimens. Following on this development, study of oxygen isotope ratios is now underway in (i) Precambrian kerogens, (ii) representative suites of Phanerozoic materials, and (iii) specimens subjected to laboratory isotope-exchange experiments aimed at exploring the possible lability of organic oxygen in sediments. These analyses will provide data allowing a systematic evaluation of the significance and preservation of biologically controlled oxygen-18 abundances in both recent and ancient kerogens. Thus far, it seems evident that the oxygen isotopic composition of sedimentary organic materials can be related to (a) the isotopic composition of the water available to the organisms and (b) some aspects of the metabolism of the organisms.

ALTERATION PATHS OF SEDIMENTARY ROCK ORGANIC MATTER DURING BURIAL

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Precambrian sediments are occasionally rich in carbonaceous material. Many excellent examples of well-preserved, carbon-rich shales and cherts dating back to over 3.6 g.a. have been studied in South Africa and Australia. Recognizable morphological remains of procaryotes have been found in numerous outcrops. Unfortunately, the nature of the chemical remains in the carbonaceous material does not permit a definitive characterization of this material to be performed. The objectives of the research being undertaken are (1) to study the pattern of catagenesis resulting from the burial of organic matter in the stratigraphic column over geologic time and (2) to devise recognition patterns which could help differentiate residual carbon compounds which were originally synthesized biologically from those which have been synthesized abiologically during the early history of the earth.

The majority of the studies have been performed by taking recent sediments, drying them and subjecting either the entire sediment or the extracted proto-kerogen to temperature regimes from 60-500°C over a period of 1 to 15,000 hours (625 days), in closed pyrex vessels. Other studies have been performed by mixing the separated proto-kerogen with defined minerals, to evaluate the role of inorganic substances in the preservation of organic carbon compounds. Measurements of Proterozoic and Phanerozic carbonaceous sediments have also been conducted. Volatile, extractable and non-extractable carbon-containing compounds have been separated and characterized. The pattern of gaseous and lipid-extractable material that form in the laboratory experiments is essentially identical to that found in Phanerozoic sediments, especially those that contain petroleum. The data clearly show that complex biopolymers will alter to geomonomers as well as geopolymers. The role of the mineral matrix is complex. Some minerals are catalytic in the alteration of the original organic matter whereas others are inhibitory. The data further show that the kinetics of organic degradation may not follow a simple first order Arrhenius model. The character of the residual kerogen can be determined by X-ray diffraction and elemental measurements. Isotopic ratio measurements of the kerogen can help to identify a biological component of the kerogen.

THE IMPORTANCE OF METAL COMPLEXED AMINO ACIDS IN GEOCHRONOLOGY OF FOSSILS AND TO THE ORIGIN OF CHIRALITY

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There is a unique relationship between optical activity and life. Virtually all proteins contain exclusively the L-enantiomer of the amino acid. These same amino acids are found in fossil shells and bones and once removed from the biosphere and reside in the geosphere, they slowly change to their mirror image, the D-enantiomer (racemization). From the D/L ratio age estimates can be made of fossil material. There is no generally accepted theory for the origin of optical asymmetry though several theories have been proposed.

The loss of optical activity to a mixture of D- and L-isomers is easier to study and progress is being made in the understanding of this aspect of diagenesis. Because amino acid racemization is a chemical reaction, it is affected by temperature, the chemical state of the amino acid (free or bound in peptides or proteins), the presence or absence of water, and metal ions (particularly transition state metals), the pH of the environment and the presence of bases and acids other than the conjugate base or acid of water. Competing reactions (e.g. hydrolysis, deamination, oxidation, etc.) play an important role as well. There is some evidence that even different species show different rates of racemization of amino acids (at least with shells) although this appears not to be the case with animal bones.

In determining the age of fossils by this method, it is critical that factors affecting the rate of racemization be very well understood and appreciated. Unfortunately this has not always been followed. It is now realized that without water, no significant racemization occurs with free amino acids, dipeptides, albumin or bone collagen. Unless hydrolysis of peptide bonds occur with proteins little or no racemization occurs. It is understood now why amino acid bound in peptides are the fastest to racemize. It is not the formation of a diketopiperazine intermediate as some have claimed, but rather the result of an intramolecular base effect.

Transition state metals, when complexed to the amino acid, show marked influences on racemization. We have recently shown that Ni(II) retards racemization while Co(III), Cr(III), Pt(II), Pd(II) and Cu(II) enhance racemization. Deuterium exchange with amino acids complexed to Co(III) occurs 6.6 times faster than racemization. Different diastereomers racemize at different rates, e.g. Δ-trans $[Co(L\text{-ala})_3]$ racemizes 4.6 times faster than the Δ-cis isomer. $[Co(III)(ala)_3]$ complex racemizes 126 times faster than free ala. There is some indication that the complex $[Ni(D\text{-ala})_2]$ is less water soluble than $[Ni(L\text{-ala})_2]$ which has important implications to enriching the "primordial soup" with the L-amino acid. Nickel was in rich concentration in the earth's crust during the early formation of life on earth.

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THE ORIGIN AND EVOLUTION OF MICROBIAL ENDOLITHS

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Microbial endoliths are microscopic prokaryotes and eukaryotes which share the common property of penetrating hard carbonate substrates by chemical dissolution. In so doing, they leave specific traces of their activity as boreholes whose morphology conforms closely to that of the organism. Such endolithic trace fossils are known to occur in rock and skeletal fragments throughout the Phanerozoic. Prior to the start of our research program the oldest known endoliths were Ordovician in age. We have begun a search for the earliest occurrence and evolutionary development of the endolithic habit. Petrographic thin sections of Cambrian and Precambrian rock are searched with high resolution light microscopy and photographed. Certain substrates are cast in plastic, the rock dissolved, and the borehole replicas studied by scanning electron microscopy. We are thus engaged in the discovery of new life forms in the Earth's early history. We relate them to the most comparable Phanerozoic and modern taxa on the basis of morphological and sedimentological evidence, determine their paleoecological relationships, and estimate their impact on the early global cycling of carbon.

Precambrian endoliths were discovered (by S.E. Campbell) in silicified ooids of the Eleonore Bay Formation, eastern Greenland (570-700 x 10^6 yrs). They are most comparable in size and morphology to modern endolithic blue-greens of the genus Hyella (cyanobacteria), a common borer of modern ooids, and possibly Pleistocene and Cambrian ooids as well. Thus it was determined that the origin of microbial endoliths predates the appearance of the skeletal bearing metazoans in the fossil record. We have also found endoliths within lower Cambrian ooids (Sardegna) which retained their carbonate mineralogy. It is therefore possible that older (Precambrian) carbonate rocksmay still bear traces of endolith activity. The oldest known endolith body fossils were Silurian prior to the discovery of silicified Cambrian brachiopod shell containing boreholes and organisms (by S. Awramik, consulting geologist). Work (by S. Golubic) on modern stromatolites of Shark Bay, Australia showed that lithification of Entophysalis stromatolites is essentially a seasonal phenomenon. The stromatolite building microflora is partly to completely destroyed by carbonate precipitating within their extracellular envelopes. The newly hardened surface is then colonized and bored by endoliths. Recolonization by Entophysalis mat starts another cycle. Assuming that this is a valid model for the growth of Precambrian Eoentophysalis stromatolites it now appears that these silicified microfossils comprised residual pockets of organisms that escaped obliteration by lithification during the same season of their genesis, rather than by later diagenetic alteration. If so, any Precambrian endoliths present had a similar preservation potential. Continuing research will address this problem, as well as the question: how old are the oldest endoliths?

ORGANIC CHEMICAL GRADIENTS IN LAMINATED CYANOBACTERIAL MATS FROM SOLAR LAKE, ISRAEL

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In the shallow water zone of Solar Lake, a continuous sequence of laminated cyanobacterial mats about 80 cm. thick is present. The oldest mats date from 2500 yrs b.p.

The ORGAST project members have concentrated their initial research on a few top mat sections (0-3, 3-10, 10-20 mm), a sample from the black sulfide reduction zone and several samples from the green colored older mats. Data were obtained about pyrolysis characteristics, carbohydrate components, several classes of lipids, carotenoid pigments, and ether and ester bound lipid moieties. Steep gradients were observed in the top mat sections. Some of these results and additional information on these sections will be presented. The major topic presented will be the further characterization of the gradients in the top mat.

A more detailed sectioning of the upper 20 mm of the algal mat resulted in 12 layers which were characterized by light and electron microscopy and also subjected to chemical analysis. The layers were analyzed by pyrolysis mass spectrometry and pyrolysis gas-liquid chromatography/mass spectrometry (EI and CI modes) to evaluate gradients in biopolymers such as proteins, peptidoglycane, storage carbohydrates and sheath material.

Lipid class profiles were obtained by capillary gas-liquid chromatography/mass spectrometry of total base hydrolyzable lipid fractions analyzed as mixtures of hydrocarbons, ketones, methyl esters and acetates with aliphatic, steroid and triterpenoid carbon skeletons.

The results will be discussed in reference to the microbial ecology of the mats. Possibilities for extrapolation to other cyanobacterial mat systems and to fossil algal mat sequences will be evaluated.

GEOCHEMICAL ANOMALIES NEAR THE CRETACEOUS-TERTIARY, EOCENE-OLIGOCENE AND PERMIAN-TRIASSIC BOUNDARIES

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As an explanation of an iridium anomaly found initially in sediments near Gubbio, Italy, it had been hypothesized that an asteroid or other large-body extraterrestrial impact might be linked to the Cretaceous-Tertiary (C-T) mass extinctions of life about 65 million years (m.y.) ago. The purpose of the present program is to critically test if that iridium anomaly did result from a bolide impact (and the character of such a bolide), if such an impact can be definitely linked to mass extinctions, if bolide-related mass extinctions were repetitive, and if bolide impacts have been responsible for major shifts in the evolution of life.

The C-T Ir anomaly has been found world-wide in about 37 different sites, 25 by our group and 12 by five other laboratories. Platinum, Au and Ir ratios in a bulk sample of the Danish C-T boundary agree exactly with values of CI chondrites (within the 6% measurement uncertainties of the latter) and are much different than the ratios usually obtained for terrestrial materials. X-ray diffraction and oxygen isotopic ratio measurements by M. Kastner have shown respectively that C-T boundary clays in Denmark and a core from DSDP Hole 465A in the Pacific Ocean were authigenic in contrast to clays above and below the boundary which were detrital. The world-wide distribution of the Ir anomaly, the exactly chondritic ratios of other noble elements associated with the Ir and the authigenic nature of the boundary clay strongly confirm an impact of a large extraterrestrial object as the source of the Ir. In our studies of 26 marine C-T sections an Ir anomaly was always found within 10 (and usually within 2) cm of the stratigraphic position (or center of the range) where paleontologists or geologists independently identified the C-T boundary. No significant Ir anomaly was found elsewhere except near the Eocene-Oligocene boundary. Thus the link between extinctions in the marine realm, particularly of plankton, is confirmed. Intensive studies in the continental realm are in progress. A second Ir horizon, associated with microtektites (about 34 m.y. old) and some (but not mass) extinctions, has been observed in three deep-sea-core sections (two by our group) of the Late Eocene epoch. Further intensive studies are in progress of many other sections from this time horizon. A study of the Permian-Triassic boundary (about 215 m.y. old) in China shows an authigenic layer with unusual abundances of many elements but with Ir < .055 ppb. Although it is most likely that such a layer has a volcanic origin, the possibility that it could arise as the result of a high-speed-comet impact is being investigated. Studies are being made of Ir and other element abundances in Pre-Cambrian sections (3.77 billion years old) to determine or obtain a limit in the average rate of meteoritic bombardment at that time.

SESSION VIII

EARLY BIOLOGICAL EVOLUTION

MICROBIAL MATS AND EARLY EVOLUTION

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Many paleontological studies including those comparing ancient stromatolites with modern microbial mats and stromatolites suggest that surface sedimentary deposition since the early Archean has been modulated by microorganisms. Since 1977 we have been studying laminated microbial communities that form desiccation polygons in a lagoonal complex north of San Quintin at Baja California del Norte Mexico. The communities contain both oxygenic and nonoxygenic photosynthetic microbes and are a source of emission of reduced trace gases to the atmosphere. Fine structure studies of the in situ community coupled with laboratory isolations have revealed a wealth of bacteria and a few protists in intimate association with sediment particles and protokerogen. Remarkable bacterial associations, such as bacteria-inside-a-bacterium and well developed sheath communities suggest that bacterial interactions of the sort hypothesized to be relevant to the origin of eukaryotic cells have been observed. This continuing research, the goal of which is the reconstruction of the major evolutionary trends in the early history of life, includes as complete as possible a description of the organismal and mineral components of this microbial mat.

The influx of terrigenous sediment and fresh water during the floods of 1979 and 1980 altered profoundly the biotic composition of the mat but did not destroy its laminated fabric. Light and electron microscopic observations as well as field studies before, during and after the large floods will eventually permit the assessment of the preservability of such structures as well as their relationship, if any, to ancient laminated carbon-rich cherts and stromatolites.

Evolutionary Relationships in the Microbial World

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Two special concerns of studies in planetary biology are the processes behind the origin and evolution of life and the effects of these same processes on the terrestrial environment. Integral to these goals is the long-standing need to determine the relative evolutionary position of the various microorganisms. Such a natural history can provide a background of biological facts against which one can evaluate proposals concerning the position in geological time of such key evolutionary events as the emergence of photosynthesis, the development of aerobic metabolism, etc. Macromolecular sequence data from ribosomal nucleic acid molecules is a powerful tool for deducing the required evolutionary relationships. It is a bonus that the same data can also be used to study the structure of the ribosomal RNAs. Understanding the constraints that govern the evolution of new structures in nucleic acid molecules is likely to be essential in bridging the gap in our knowledge which separates the processes of chemical evolution from the emergence of the first true organisms.

Considerable progress has been made. This includes: (1) development of efficient procedures for sequencing 5S rRNA and the use of these procedures to determine seventeen new sequences; (2) the elucidation of universal secondary structural features in eucaryotic 5S rRNA; (3) the discovery that archaebacterial 5S rRNAs exhibit a variety of secondary stuctures that are distinct from those that are characteristic of eubacteria or eucaryotes; (4) the discovery of an unusual 5S rRNA that contains a 108 nucleotide insertion in its interior; (5) development of an automated system for analysis of 16S rRNA catalog data; (6) generation of summary dendrograms from over 200 bacterial strains that gave the first experimentally-based overview of bacterial evolution; and (7) completion of a Monte Carlo simulation system that promises to provide further insight in interpeting the 16S rRNA data.

Major phylogenetic conclusions of the RNA work to date include (1) confirmation of the long held view that anaerobic genera preceded the aerobes; (2) the discovery that the photosynthetic phenotype is quite old; (3) the finding that the mycoplasmas are related to a specific subgroup of Clostridia and hence unlikely to be of great significance in early evolution; (4) confirmation of the endosymbiotic hypothesis as it pertains to chloroplasts and most importantly; (5) the demonstration of a fundamental dichotomy in the bacterial world that divides it into two classes of procaryotic entities, the eubacteria and the archaebacteria.

MOLECULAR EVOLUTION AND STUDIES ON *METHANOBACTERIUM FORMICICUM*

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The goal of our research program is two-fold: 1) the study of the archaebacterium *Methanobacterium formicicum* and 2) the development of improved techniques for the evolutionary analysis of nucleic acid sequences from extant organisms. With respect to the latter, natural selection for biological function and the nature of the genetic code have resulted in experimentally measurable constraints on gene and messenger RNA structures. Methods for using these measured constraints to extract evolutionary information from pairs of homologous genes will be discussed. The archaebacterial hypothesis states that there exists a major group of organisms which represent an ancient line of evolutionary descent distinct from the eukaryotes and prokaryotes, but sharing certain characteristics with each of the latter two kingdoms. Based on differences in 16S ribosomal RNA sequences, tRNA structure, cell wall composition and the chemical nature of membrane lipids, the archaebacteria are thought to include methanogenic bacteria, extreme halophiles and extreme thermoacidophiles. Our objective is to test this hypothesis by examining gene fragments of the archaebacterium *Methanobacterium formicicum.*

The evolution of the genetic code has been clarified by the discovery of amino acid codes in mitochondria that differ from the universal (nonmitochondrial) code. Mitochondrial codes use U in the first position of several anticodons to pair with U, C, A and G in codons. Starting from this primitive coding system a scheme is suggested which explains simply how the code could have evolved from 16 anticodons for 15 amino acids to its present day form of 64 codons for 20 amino acids. The structure of the present-day code permits a natural classification of the experimentally observed nucleotide substitutions between pairs of homologous nucleic acids descended from a common ancestral gene into subgroups reflecting constraints on function. The evolutionary information extractable from the experimental patterns among subgroups is shown for the genes of cytochrome *c*, alpha and beta hemoglobin, and for the genes that code for the VP1 and VP2 capsid proteins of the murine polyoma virus, simian SV40 virus, and human BK virus. To study *Methanobacterium formicicum,* we are in the initial phases of establishing a gene library of the entire genome of this organism in an *Escherichia coli* K-12 host using recombinant DNA techniques. From this library we will subclone a gene for an aminoacyl tRNA synthetase. In vitro studies are in progress which will establish whether any of the *Methanobacterium formicicum* enzymes is capable of heterologous aminoacylation of tRNA from *Escherichia coli.* The methanobacterial gene specifying the synthetase will be selected for in an *E. coli* strain mutant for the synthetase. The gene library can also be probed for tRNA genes. Sequencing the chosen archaebacterial gene should help define archaebacterial transcriptional promotor and terminator sequences. This work should also contribute to the understanding of specificity of tRNA charging. The gene library can also be used to search for genetic functions involved in methanogenesis. The most readily approachable are genes carrying out the biosynthesis of two coenzymes--coenzyme M and the flavinoid pigment F_{420}.

Determining the Origin and Early Evolution of Living Organisms Based on Protein and Nucleic Acid Sequence Data

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Many proteins and nucleic acids are "living fossils" in the sense that their structures have been dynamically conserved by evolution over billions of years: recognizably related molecules are found in eukaryotes and prokaryotes. Such molecules are believed to be of common evolutionary origin, having evolved by many small changes in the sequences. The positions in the aligned sequences can be used as traits in numerical taxonomy. From a comparison of the chemical structures in each sequence, an evolutionary scheme is deduced. These methods have proved quite successful: the 5S ribosomal RNA molecules elucidated from a wide variety of species give a comprehensive framework, as described below. It remains to add the hundreds of other phyla and major groups, to identify transfers of genetic material, and to make more precise computations using molecules with more information. Using the order of branching worked out from the sequences along with additional information on metabolic capacities and morphology, a very interesting evolutionary scheme will finally be worked out.

The comprehensive tree that we derived from one molecule, 5S rRNA, unquestionably confirms the separate origins of the cytoplasmic constituents, the mitochondria and the chloroplasts of eukaryotes from three different prokaryote lineages, thus confirming the symbiotic theory of the origin of the organelles. The chloroplasts of higher plants derive from an ancestor of Anacystis and Prochloron; the mitochondria, from the purple nonsulfur bacteria; and the cytoplasmic constituents, from the archaebacterial line including Thermoplasma acidophilum and Sulfolobus acidocaldarius. There are a number of additional molecules from which substantial trees can be constructed, including 4Fe-4S ferredoxin, c-type cytochromes, and cytochrome c' from bacteria, 2Fe-2S ferredoxins of blue-greens and chloroplasts, and 5.8S ribosomal RNA sequences from eukaryotes. Essentially complete sequences of the principal ribosomal RNAs from the large and small subunits are known from a diverse group of prokaryotes, eukaryotes, and eukaryote organelles. An examination of the consistency of the trees supports the hypothesis that the transfer between species of genes for molecules of fundamental importance followed by persistence in evolution is a rare occurrence.

The rate of sequence analysis has reached an explosive stage due to the recent breakthrough in nucleic acid sequencing techniques. There are now well over 1,000,000 nucleotides sequenced and this database is at least doubling every year. There is a great deal of information that has not been examined for phylogenetic inferences. The availability of the data is not the problem, as we are currently maintaining nucleic acid and protein sequence databases available on magnetic tape and through telephone access to a retrieval system on our computer. The problem now is to evaluate and provide standardized computer methods in a form practical for the systematist to use in phylogenetic analysis. It is possible to provide programs as well as the data through telephone access to computers elsewhere. We will discuss the feasibility of a collaboration of scientists interested in providing, evaluating, and maintaining computer programs for scientists who will be investigating the evolutionary process.

A LOW MOLECULAR WEIGHT, ARCHAEBACTERIAL ADENOSINE TRIPHOSPHATASE

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The membrane bound, energy transducing adenosine triphosphatases (ATPases) consist of two major structures. One, F_1, consists of 5 subunits whose aggregate molecular weight is about 380,000 daltons. The other, F_o, is intimately associated with the membrane and consists of three subunits whose combined molecular weight is approximately 150,000 daltons. The ubiquitous distribution of these ATPases among prokaryotic and eukaryotic organisms, and their nearly similar structural and functional properties, suggest a highly conserved structure which arose early early during evolutionary history. Yet such a notion does not seem reasonable given the complexity of the ATPases and a process involving evolution from something simpler seems more attractive.

We have been examining a number of halobacter for the presence of ATPase activity with the assumption that such organisms might possess a less highly evolved enzyme. We have detected ATPase activity in a number of extremely halophilic bacteria, and the enzyme from one of these, Halobacterium saccharovorum, has been partially purified and characterized. The enzyme exhibits many similarities to the proton translocating ATPase from other cells (i.e. K_m(ATP), K_i(ADP), latency of activity, cold sensivity, and lack of substrate and divalent cation specificity). However, the solubilized ATPase (i.e. F_1) has an apparent molecular weight of about 120,000 daltons as judged by gel filtration. Whether this low molecular weight represents a 5 subunit structure where each subunit has a lower molecular weight than found in the subunits from other F_1 structures, or the F_1 from H. saccharovorum is an ATPase consisting of fewer subunits is not clear at this time. Either alternative would be consistent with a more primitive enzyme than that found in other organisms and suggests that the halobacteria may provide information on the origin and evolution of the energy transducing ATPases.

A YEAST-LIKE FIRST EUKARYOTE ?

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The most dramatic recent advances in our understanding of the origin of cellular life and of eukaryote life have been made as a result of comparing the nucleic acids of divers cells and cell components. These origins remain controversial, though speculation has been directed into better defined channels by this research. At a less basic, but equally important, level the taxonomy of modern bacteria has been revolutionized by the work of Woese and his collaborators with catalogued oligonucleotides from 16S rRNA. The phylogenetic trees constructed from this and other comparisons indicate that a character must be derived (not indicating relationship) when it occurs on independent branches (necessarily tertiary branches), thus possessing the capability, when sufficient and appropriate organisms have been examined, of clarifying the nature of all but the first two branching of cellular life. Current phylogenetic trees compare relatively few organisms, because such research is time-consuming, and therefore have some important branches in regions of low, error-prone, homology. Hybridization techniques are the most rapid, and could be used to screen potential subjects for cataloguing and sequencing. We are developing a new method of 25S rRNA hybridization and exploring its use in the classification of basidiomycetous yeasts. One theorizer has proposed that yeasts were the first eukaryotes. We think this unlikely; molecular comparison is a sufficiently powerful tool to show whether unicellularity in the eufungi is a derived character.

The unique yeasts of barren sites in the Dry Valleys of Antarctica have been shown by DNA-DNA homology to belong to several species probably originating outside of this habitat, though one species has evolved into several varieties within the Dry Valleys. The congeners of these sexless (anamorphic) yeasts were shown by cDNA-25S rRNA homology (by a new technique made possible by adding poly A tails (ala Engel and Davidson, 1978, Biochem. 17: 3883) to 400-600 mer fragments of isolated 25S rRNA, duplexing the tails with oligo d(T) and using reverse transcriptase (see Verma, 1981, The Enzymes 14: 87) to prepare tritiated cDNA) to be *Filobasidiellas*, a teleomorphic (sexy) genus which is not psychrophilic, but may have other preadaptations (to be examined) to Dry Valley life. In a three-dimensional map of cDNA-25S rRNA homology, the genera *Filobasidiella, Filobasidium, Leucosporidium*, and *Rhodosporidium* (the known teleomorphic basidiomycetous yeasts excepting *Aessosporon* and *Sporidiobolus*) are points enveloped in spheres of standard deviation, but separated by at least twice the standard error of difference. This technique defines genera and probably extends to the orders of traditional (but controversial) schemes, since *Aessosporon* (Uredinales) shows 44% homology to *Rhodosporidium*, but none to *Filobasidium* (Tilletiales). Regions of low DNA and RNA homology are not mappable, in part because of the large errors associated with low homology, to which all molecular comparisons are subject, but also because different parts of the probed molecules are duplexing with the probe. The 5S rRNA trees of Hori and Osawa (1979, PNAS 76: 381), compared with the work of Bicknell and Douglas (1970, J. Bact. 101: 505) on 25S rRNA homology (by the method of Gillespie, 1968, Meth. Enzymol. 12B: 641) in *Saccharomyces sensu lato* suggests that low homologies become higher when shorter rRNA molecules are used. Our technique would be a useful screen in establishing the bona fides of subjects for sequencing of smaller rRNAs. Sequence comparison, though still requiring interpretation, allows linear comparison of whole molecules.

OXYGEN REQUIREMENTS FOR LIPID SYNTHESIS IN MICROORGANISMS

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Life on Earth presumably originated in an essentially anaerobic environment. At some time, perhaps as much as 3.3 billion years ago, the process of oxygenic photosynthesis was "invented" and oxygen gradually accumulated in the atmosphere. What the history of atmospheric oxygen was before this period is obscure. However, from the standpoint of evolutionary development, the biological production of oxygen was crucial. Classical evolutionary thought would suggest that anoxygenic metabolic pathways are more "primitive" than oxygen-requiring ones. Indeed, the presence of oxygen-requiring metabolic processes in eucaryotes has been used as an argument that these organisms appeared after the atmosphere became oxygenic. We have been studying unsaturated fatty acids and sterols, compounds known to require atmospheric oxygen for their formation in eucaryotes. However, in both cases there exist alternative anoxygenic pathways resulting in functionally equivalent compounds, i.e., monounsaturated fatty acids and hopanes. Additionally there appears to be some phylogenetic relationship; procaryotes predominantly utilize the anoxygenic mechanisms, and eucaryotes the oxygenic ones. Even in the eucaryotes, however, little attention has been paid to the levels of oxygen necessary to carry out the syntheses of unsaturated fatty acids and sterols. In the simple eucaryote, S. cerevisiae, we have demonstrated that the oxidative desaturation of palmitic acid and the conversion of squalene to sterols occur in the range of 0.002 PAL to 0.01 PAL. Thus biological systems interacting with oxygen in eucaryotes could have been operational relatively early in biological evolution, and these "aerobic" processes more primitive than previously thought.

Recent work has continued on the oxygen-requiring processes of lipid synthesis in microorganisms. The conversion of squalene to ergosterol, a metabolic process involving at least five individual oxygen-requiring enzymes, has been investigated in yeast. We have developed an *in vitro* system for the conversion of squalene to lanosterol in which squalene is preferentially converted to lanosterol by particulate preparations of anaerobic cells. In this system, addition of the inhibitor AMO-1618 results in accumulation of 2,3-oxidosqualene and allows the squalene epoxidase, the first oxygen-requiring step, to be investigated. The "apparent" half-maximal activity for the epoxidase is reached at an oxygen concentration equivalent to 0.01 PAL. *In vivo* studies on the oxygenation of anaerobic cells have shown that the epoxidase activity doubles at a level of only 0.001 PAL. In other studies, we have found that this low level of oxygen completely stabilized the palmitoyl-CoA desaturase system in these organisms. Additionally, we have recently initiated studies on the formation of mono- and polyunsaturated fatty acids in cyanobacteria. Using a culture of Nostoc sp. in which their oxygen-generating photosystem II is poisoned by DCMU, coupled with the presence of Na_2S, we have found that these desaturations, which require atmospheric oxygen, occur at levels of oxygen below 0.012 PAL.

PRIMARY AND SECONDARY ENERGY CONVERSION IN HALOBACTERIUM MEMBRANES

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A distinct milestone in the origin of life is the establishment of biological individuality, i.e. the delimitation of space to include a specific group of molecules and exclude others. It is only a small step from here to acquire the ability to maintain a chemical environment within this space which is different from the surroundings, and which is kept constant in the face of outside influences. It is reasonable to believe that it was a proto-membrane, and vectorial catalysts in it, that made this step possible. In this context studies of simple energy conversion systems in present-day biological membranes are needed to develop models for the membrane energetics of a primitive cell. It is fortunate that such systems, based on light energy utilization, exist in the halobacteria, which are thought to be, as members of the archebacterial group, organisms with preserved ancient properties. We have identified mechanisms for sodium and chloride transport in halobacterial membranes.

Sodium ions are removed from halobacterial cells via a coupled primary/secondary transport system consisting of a proton loop (bacteriorhodopsin) and a sodium loop (sodium/proton antiporter). The activity of these loops results in the recirculation of extruded protons and the continued extrusion of sodium. The antiporter appears to be electrogenic in that 2 protons are exchanged for one sodium. It is a gated system, which results in rectification of the sodium flux in the physiologically meaningful (outward) direction. The electrical potential which develops has two important consequences. One is that potassium is transported inside, probably by a passive mechanism, so that sodium is replaced by potassium. The other is that chloride is passively lost, resulting in net loss of salt and therefore water and volume. This chloride is regained by a second active transport system (halorhodopsin), which we find functions as a direct, inward directed chloride pump. The combined action of these transport systems results in the maintenance of sodium/potassium gradients across the membrane and constant volume.

LIGHT ENERGY CONVERSION IN HALOBACTERIA

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We are investigating the structure and function of a new biological energy transducing system embedded in the cell membrane of Halobacteria which live in natural brine pools. Halobacteria are now clasified as Archaebacteria implying that they are among the oldest living cells. Therefore these organisms are of special interest for the evolution of life and survival in extreme enviroments. Bacteriorhodopsin functions as a light driven proton pump which ejects protons from the cell. The resulting electrochemical potential across the cell membrane is chemiosmotically coupled to energy requiring processes such as ATP synthesis, ion and aminoacid transport, and locomotion. The purpose of our research is to understand the structure and function of this pigment, which is the simplest and presumably earliest ion pump and light energy-transducing pigment known.

We are using conventional and time-resolved absorption spectroscopy in the visible and U.V. range, routine biochemical techniques and recently pulse radiolysis to characterize the pigment. We have determined Lys-216 as the retinal chromophore-binding site and shown that the earlier described site at Lys-41, observed only under special conditions, is presumably an artifact but can be used to obtain information on the 3-dimensional structure of the protein. Ultraviolet absorbance changes during the bacteriorhodopsin photocycle indicate that tyrosine group(s) undergo transient deprotonation. We have selectively nitrated one tyrosine residue that affects spectroscopic and photocycle kinetics. The data suggests that this residue is involved in a proton transfer reaction. We are trying to locate this group in the sequence and, if possible in the 3-dimensional structure,either by refinement of existing structural data or after labeling with heavy atoms.

We have recently isolated from natural brines several new strains, which carry similar or identical pigments, which will be compared, using our standard techniques, to bacteriorhodopsin and to the recently discovered halorhodopsin to see if variations in the structure occur and which components are essential for function.

THE CRYPTOENDOLITHIC MICROBIAL COMMUNITY: A "CLOSED" ECOSYSTEM IN NATURE

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Cryptoendolithic microorganisms living in rocks of the Antarctic cold desert are highly specialized because they are adapted to an extreme environment. Yet the structure of this ecosystem is simple. It consists only of primary producers, consumers and decomposers; secondary consumers and predators are absent and the number of species is very small. Such a system may be regarded as a model for primitive, archaic conditions. The physical and chemical components can be expressed in comparatively few parameters and this makes it suitable for quantitative study.

This ecosystem can exist in balanced condition due to the fact that it is closed to a considerable degree. Ecosystem closure can range from adiabatic isolation (closed to the flow of matter and energy) to biological closure (Maguire et al., Microcosms in ecological research, U. S. Dept. Energy, Symp. Ser., 52, 1980). The cryptoendolithic ecosystem is biologically closed on the biological timescale (but is open on the geological timescale). At the same time, flow of matter is significantly restricted. Preliminary results indicate that an inner CO_2 pool exists in the endolithic airspace which controls photosynthesis. Keeping biomass below a certain limit (by regulating primary productivity) is a necessity in the physically limited space of the cryptoendolithic microenvironment.

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